Direct Partial Oxidation of Methane to Methanol over Designed Heteropoly Catalysts

Final Report

by

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SUMMARY

The partial oxidation of methane has been studied on heteropoly oxometalates with Keggin structure anions of various compositions. Nitrous oxide and oxygen have been employed as oxidants. Reaction temperatures from 450 to 600°C, residence times of 5 to 30 g. cat./ml min^{-1} and CH_4/N_2O ratios of 1 to 9 have been employed. The catalysts examined, $HPW_{12}O_{40}$, $HPW_{10}MO_2O_{40}$, $HPW_{10}V_2O_{40}$, $HPMo_{12}O_{40}$, $HPMo_{10}W_2O_{40}$, $HPMo_{10}V_2O_{40}$ were supported on high area silica and activated in helium, air or hydrogen. Salts of $HPMo_{12}O_{40}$ were also prepared by direct exchange of the proton by the cations on the supported acid.

The selectivity to partial oxidation products methanol and formaldehyde was found to be inversely related to the conversion of methane. Of those catalysts tested, 12-molybdophosphoric acid, $HPMo_{12}O_{40}$ appears to be the most effective. Substitution of the protons by heavier cations was found to reduce the selectivity to partial oxidation products. The effect of catalyst loading on the support was also examined with $HPMo_{12}O_{40}$.

Low residence times (< 10g.cat/ml. min^{-1}), low temperatures (< 500°C) and high CH_4/N_2O ratios (9/1) were found to favour the selectivity to partial oxidation products tested. While selectivities approaching 100% to partial oxidation products can be obtained, conditions which reduced the conversion to less than 1% were required.

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(a) Introduction

Objectives

Catalysts based on heteropoly oxometalates will be selected, prepared and tested for the partial oxidation of methane to methanol.

Background

It is well-known that the selective removal of hydrogen atoms from methane is a difficult process. Although the thermodynamics is highly favourable for complete oxidation, production of formaldehyde and methanol is also thermodynamically allowed (Fig. 1). Not surprisingly there has been increased interest in recent years in the partial oxidation of methane. Three reviews on this subject have appeared in the last twelve months (1-3). Much of the recent work on the partial oxidation of methane has involved the O^- ion. Early gas phase studies (4) showed that this ion was capable of stripping a hydrogen atom from an alkane

$$O^- + RH \rightarrow OH^- + R$$

Subsequently, Lunsford and coworkers (5,6) have shown that low molecular weight alkanes can be partially oxidized at room temperature over MgO with nitrous oxide, apparently through the abstraction of hydrogen atoms by O^-, followed by reaction of alkyl radicals with O^{2-} ions contained on the surface of MgO. Further work by Lunsford (7-11) has shown that methane and ethane can be catalytically oxidized by N_2O over a molybdena/silica catalyst and most recently (12) that conversion of methane to ethylene and ethane can be achieved with O_2

as the oxidant over a lithium-promoted magnesium oxide catalyst. Somorjai and coworkers have recently studied the kinetics of the partial oxidation of methane with nitrous oxide over both molybdena/silica (13) and vanadia/silica (14) catalysts.

The gas-phase radical formation during the reactions of methane, ethane, ethylene, and propylene has been shown (15) to be dependent on the bond strength of the weakest C-H bond, the presence of particular radical-forming sites on the catalyst surface, and the ability of the radicals to desorb or take part in further surface reactions. The influence of experimental conditions on the formation of O^- ions from N_2O adsorption on reduced grafted molybdena/silica and the role of these ions in surface charge-transfer reactions has also been analyzed recently (16-17).

Anderson and Tsai (18) have recently reported the results of studies of the oxidation of methane on H-ZSM5. Conversion of methane up to 2.7% and methanol product compositions to 3.6% were obtained but formaldehyde, lower olefins (ethylene and propylene) and C_6-C_{12} aromatics were also produced. However the product in all cases contained 68-78% of carbon dioxide.

The oxidative dimerization of methane over lanthanum oxide (19) and over bismuth oxide (20) catalysts has also been reported recently.

In this laboratory the structural, surface, and heterogeneous catalytic properties of heteropolyoxometalates are being studied by a variety of techniques (21-24). This work has concentrated on those heteropoly compounds with Keggin structure. These are ionic solids in which the anion has a high molecular weight, cagelike structure, with an atom such as phosphorus, silicon, or arsenic at its centre and four oxygen atoms tetrahedrally arranged around the central atom. Twelve octahedra, with an oxygen atom at each of the vertices and a metal atom such as molybdenum, tungsten, or vanadium, at each of their

centres, surround the central tetrahedron and share oxygen atoms with each other and the former (Fig.2). This is referred to as the Keggin structure and the anions with such a structure as Keggin Units (KU). Three different types of oxygen atoms are present; one terminal, protruding from the anion, one bridging between two peripheral metal atoms and the other bridging between the central atom of the anion and the peripheral metal atoms. In the case of heteropoly acids with Keggin structure the protons are each surrounded by four water molecules and hydrogen bonded to the oxygen atoms of two water molecules at a given time. The protons of the water molecules are in turn hydrogen bonded to the terminal oxygen atoms (Fig.3). The secondary structure of the heteropoly acids with the proton and anion configurations connected is shown in Fig.4.

In particular it has been shown by temperature-programmed-desorption, -reduction, and -exchange experiments (21-23) that water is desorbed at two temperatures, that at the higher temperature resulting from the abstraction of oxygen from the heteropoly anion by the acidic protons. Further, photoacoustic FTIR studies (23,24) have shown that the dehydration of methanol on 12-tungstophosphoric acid involves the methylation of anionic (presumably terminal) oxygen atoms. Extended Huckel calculations (25) have shown that the acid strength of the protons in the heteropoly acids is inversely related to the charge on these terminal oxygen atoms, while the catalytic activity in oxidation processes appears to be proportional to the strength of the anionic peripheral metal-oxygen bond.

Earlier work from this laboratory has shown that 12-tungstophosphoric acid (26-27) and its metal and ammonium salts (27-29) are capable of converting methanol to hydrocarbons ($> C_1$) presumably via a route in which the anionic

terminal oxygen atoms are methylated. In contrast, with 12-molybdophosphoric acid, methanol is primarily converted to oxidation products, principally carbon monoxide. In the former case higher reaction temperatures, for example, those greater than 400°C produce a reaction product which is predominantly methane, rather than higher hydrocarbons. It thus appeared possible that the methylation of the terminal anionic oxygen atom may be achieved by the use of methane as reactant rather than methanol.

A number of other workers (30) have shown that certain heteropolyoxometalates are effective in oxidation processes, although no work has yet been published relating to the oxidation of methane.

In this laboratory bond order - bond energy calculations have been employed to examine the interactions of methane with simulated surfaces. Various simple mechanistic models were employed to trace the energy surface during both the adsorption and C-H bond scission. A preliminary account of this work was presented at the 35th Canadian Chemical Engineering Conference, October 6-9, 1985 (31).

Justification and Value to Canadian Economy

Canada is fortunate in having abundant supplies of natural gas. Currently approximately 25% of our production is exported, primarily to the United States. Much of the natural gas is employed in this country as a fuel in stationary applications, although there is increased use in the form of compressed natural gas as a vehicle fuel. However gasoline continues to be the most convenient combustible mixture for the latter purpose. Unfortunately methane, the major component of natural gas found in Canada, has enjoyed relatively little use as a chemical raw material partly as a consequence of its

state under ambient conditions but largely as a consequence of its resistance to selective conversion. A process for the selective oxidation of methane under relatively mild conditions (ambient pressure and temperatures less than 600°C) which yields a liquid product such as methanol, the latter of which could be catalytically converted to C_2 - C_6 hydrocarbons, would therefore have considerable potential economic advantages. The gaseous methane could thereby be converted into a more convenient form for use as a transportation fuel while also being more amenable as a raw material in further chemical processing.

Results and Discussion

Task 2:

The microcatalytic reaction system is shown schematically in Figure 5. Gas supplies feed through control valves, rotameters, and fine control valves. A pressure gauge (3) and pressure relief valve (4) are mounted in the line. A saturator (6) is also available in the feed line. The reactant stream passes to reactor R1 or R2 and may be passed via gas sampling valves to a gas chromatograph.

Task 3:

The heteropoly acids, 12-tungstophosphoric and 12-molybdophosphoric acids were purchased from BDH (Analar grade). The heteropoly acids with two peripheral metal acids were prepared from appropriate amounts of sodium phosphate, sodium molybdate, sodium tungstate and sodium vanadate.

The composition of the prepared acids was measured by DCP (Beckman Spectrocan Model 5) calibrated for each element by use of the sodium salts of the appropriate acids. The results are shown in Table 1 relevant to phosphorus.

TABLE 1

Stoichiometry	Measured Number of Peripheral Metal Atoms		
	Mo	W	V
$H_3PMo_2W_{10}O_{40}$	1.6	10.4	---
$H_3PMo_4W_8O_{40}$	4.4	7.6	---
$H_3PMo_6W_6O_{40}$	5.5	6.5	---
$H_3PMo_8W_4O_{40}$	7.1	4.9	---
$H_3PMo_{10}W_2O_{40}$	9.3	2.7	---
$H_4PMo_{11}VO_{40}$	10.0	---	2.0
$H_4PMo_{10}V_2O_{40}$	9.1	---	2.9
$H_4PMo_9V_3O_{40}$	8.5	---	3.5
$H_5PW_{10}V_2O_{40}$	---	7.9	4.1

Preliminary studies of these solid acids as catalysts in the partial oxidation of methane showed that the hydrocarbon was unable to penetrate to the active sites in the bulk of the solid. Separate experiments in which the solids were exposed to methane at elevated pressures up to 200 atm. showed that no appreciable sorption resulted. To circumvent such difficulties a technique to expose more of the active sites of the solid acids to methane was required. The most convenient method appeared to involve the use of a high surface area support. Experiments with a number of such supports showed that a high area silica (Grace-Davison grade 400, 740 ± 20 m^2g^{-1}) was effective for such purposes. Consequently all results reported here have been obtained with silica-supported catalysts.

Certain monovalent cation salts of heteropoly acids have been shown in this laboratory to possess microporous structures (32-34) and consequently surface

areas considerably higher than those of the parent acids. While the solid acids have been shown to possess areas of less than 10 m^2/g, the microporous salts were found to have areas as high as 200 m^2/g. Experiments in which these microporous salts were tested as catalysts for the oxidation of methane showed that these solids suffered from the same difficulty as the parent solid acids, that is, a less than ideal accessibility of methane to the active sites. Unfortunately insolubility of the microporous salts prevented the direct coating of silica particles with such salts as was possible in the case of the parent acids. This difficulty was, however, circumvented by the preliminary preparation of the supported heteropoly acid followed by exposure to appropriate quantities of aqueous solutions containing the desired cation.

Task 4

Catalyst samples were characterized by infrared spectroscopy, powder X-ray diffraction, differential thermal analysis, and elemental analysis (DCP).

Infrared spectra (Perkin Elmer 983) were recorded on pressed disks using KBr, primarily in the range 1500-305 cm^{-1} in order to observe the Keggin Unit structure of the heteropoly oxometalates. The powder X-ray diffractograms were measured with a Phillips diffractometer (Model PW-1011/60) using CuKα radiation. The samples were dried at 170°C before measurement. DTA measurements (Du Pont Model 99) were carried out in the temperature range 50-650°C with alumina as a reference sample, nitrogen as a purge gas and heating rate of 10°/min.

The infrared spectra of heteropoly oxometalates shows 5 or 6 bands below 1100 cm^{-1} characteristic of the Keggin structure for the anion. In particular, bands at approximately 1080 and 980 cm^{-1}, the former attributed to the triply degenerate stretch of the central XO_4 tetrahedron and the latter to

the peripheral metal atom-oxygen stretch have been used in this laboratory as characteristic of the Keggin structure. The exact position of these bands was found to vary with the relative number of peripheral metal atoms of a given type when two peripheral metal elements are contained in the anion (Figure 6). This may be used as a means of identifying both the type and number of peripheral metal atoms.

Tasks 5 and 6

As has been noted it was necessary to support the various catalysts in order to facilitate the availability of the otherwise inaccessible active sites contained within the bulk. This adds an additional variable to those normally considered in such experiments. Various loadings of 12-molybdophosphoric acid on silica were prepared and tested to determine optimum values.

The effects of pretreatment conditions, contact time, mass of catalyst, reaction temperature, and relative concentrations of methane and nitrous oxide are shown in Figures 7-12 for the 29.4% $HPMo/SiO_2$ catalyst. Although pretreatment in helium, N_2O, H_2, CH_4 and CO produced similarly shaped deactivation curves (Fig.7 a-f), with oxygen the conversion of methane initially increased in contrast to the decrease observed with the other gases used in the pretreatment. In general pretreatment in an oxidizing atmosphere (N_2O, O_2) resulted in lower steady state conversions than that in reducing gases (CH_4, H_2, He, CO) . In general, the selectivity of the CH_4 + N_2O reaction toward partial oxidation products increases with the duration of reaction.

A decrease in the apparent contact time favours an increase of the selectivity to partial oxidation products until a maximum is reached (Fig. 8). An increase in reaction temperature displaces these extrema toward lower

apparent contact time, suggesting that higher temperatures favour the subsequent oxidation of the partial oxidation products and CO.

Although it may be expected that a reduction in the thickness of the catalyst bed would favour the production of partial oxidation products, it is evident from Fig. 9 that the observations are not consistent with such an expectation. The total flow rate is evidently the dominant parameter as improved partial oxidation selectivity is obtained for large catalyst mass and high total flow rate.

The effect of the reaction temperature on the selectivity of the $CH_4 + N_2O$ and $CH_4 + O_2$ reactions on the silica support and the 29.4 HPMo catalyst is shown in Figure 10. An increase in reaction temperature leads to an increase in the production of CO_2 and a decrease in that of CO and formaldehyde, an effect which is strongly attenuated when a high flow rate is used.

Reactant composition also effects the selectivity (Fig. 11). Low values of the molar ratio N_2O/CH_4 favour the production of partial oxidation products until a maximum is reached at approximately N_2O/CH_4 equal to 0.1 under the conditions used. The CH_4 conversion increases linearly as the N_2O fraction increases from 0 to 17% while the CH_4 conversion decreases when the fraction of CH_4 increases. Evidently the selectivity is approximately inversely related to the conversion.

All of the samples listed in Table 1 were tested as catalysts for the partial oxidation of methane. The influence of the chemical composition of the anion on the catalytic properties was studied at 450, 530, and 570°C. An equimolar substrate mixture with a total flowrate of 20 ml/min was employed. It

should be emphasized that subsequent work was performed in the absence of a carrier gas. For this work only one catalysts loading, 20 wt% on silica, was employed. Catalyst samples were activated for one hour prior to the reaction in a helium stream at the reaction temperature.

The effects of anion composition and pretreatment environment are illustrated in Table 2. It may be seen that vanadium has a beneficial effect on catalyst activity, but not selectivity, while catalysts predominantly composed of tungsten as peripheral metal element are the least effective as oxidation catalysts. While there is relatively little influence of the pretreatment gas on the conversion of methane, the selectivities appear to be more susceptible to the pretreatment environment. Although an internally self-consistent trend is not immediately obvious it appears that the pretreatment gas has a stronger influence at the lowest conversions. Air and helium are apparently the least and most preferable, respectively.

As noted earlier, increase in temperature increases the conversion while decreasing the selectivity. This is illustrated in Fig. 12 for 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) (20% by wt.) supported on silica. At 520°C the conversion of methane nears 2% while the product is only 20% in liquids, almost entirely formaldehyde. In contrast, at 450°C the conversion has decreased to approximately 0.2% while the product now consists of approximately 30% methanol and 55% formaldehyde.

The effect of residence time is illustrated for the same catalyst in Fig. 13. Here the total flowrate is 10 ml/min. as compared with 20 ml/min. in the previous figure. It is readily evident that, while the conversions are higher, the selectivities are lower, for all temperatures.

The substitution of tungsten for two of the molybdenum atoms in each anion produces a small increase in conversion but a decrease in selectivity for all temperatures (Fig. 14).

The substitution of vanadium for one of the molybednum atoms in each anion produces a substantial increase in conversion at the higher temperatures but little change in the latter at the lower temperatures. The selectivity to liquid products is lowered at all temperatures by the introduction of vanadium (Fig. 15).

It should be noted, in the last three figures that, at a total flowrate of 10 ml/min. the product content of CO is very nearly constant (70 ± 10%) with respect to temperature.

As has been noted the conversion increases with residence time while the selectivity to liquid products decreases. This is illustrated, for 12-molybdophosphoric acid, at 450°C (Fig. 16). At W/F equal to 5, the conversion is approximately 0.2% and the products are entirely liquid, approximately 75% formaldehyde and 25% methanol. At a residence time of 30 the conversion has increased to 0.35% while the product is now 25% formaldehyde and 15% methanol.

With $H_3PMo_{10}W_2O_{40}$ at 450°C the trends with residence time are semi-quantitatively similar (Fig. 17) to those with $H_3PMo_{12}O_{40}$.

The influence of reactant composition with the catalyst $H_3PMo_{12}O_{40}$ at 530°C and a 40 ml/min. total flowrate is seen in Fig. 18. With increasing CH_4/N_2O ratio the conversion decreases to approximately 0.5% at a value of 9 for the former, while the liquid product increases to 40%.

It is interesting to compare the previous figure with Fig. 19 which applies to separate catalyst beds of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ arranged

sequentially at the same temperature 530°C and 40 ml/min. total flowrate. It should be noted that these two catalysts were separately supported on silica. In contrast to the previous figure, the product at a CH_4/N_2O ratio of 9 now contains 70% formaldehyde, and approximately 10% and 2% of ethylene and methanol, respectively.

Conclusions and Recommendations

1. It has been demonstrated that heteropoly oxometalates are active and selective in the partial oxidation of methane.
2. It is necessary to support the heteropoly oxometalates on a high area solid since methane will not penetrate into the bulk of these materials. It has been found possible to support the water-soluble heteropoly oxometalates on slicia of approximately 700 m^2/g.
3. It is shown that the activity and selectivity of the heteropoly oxometalates in the partial oxidation of methane varies with the nature of the central atom and peripheral metal elements in the anion.
4. The preferred catalyst for the partial oxidation of methane is 12-molybdophosphoric acid. The preferred oxidant, reaction temperature, residence time and reactant ratio are nitrous oxide, 450°C, W/F = 5-10, and CH_4/N_2O = 9/1, respectively. However, under such conditions the conversion is 0.02-0.1% and the liquid products are approximately 80% formaldehyde and 20% methanol.
5. It has been shown that the heteropoly acid, 12-molybdophosphoric acid gains increased thermal stability when supported on silica.
6. The exchange of the protons contained in the supported 12-molybdophosphoric acid with various cations, while yielding valuable mechanistic information in general produces a poisoning effect.
7. Evidence from this work suggests that methanol may be converted to formaldehyde through thermal degradation on exit from the catalyst bed. Therefore it is recommended that a study of the effect of quenching the reaction products be instituted.

8. Further to #7 it is recommended that modifications of reactor design to permit the introduction of a temperature gradient be studied.
9. Work reported here demonstrate that with many of the catalysts studied, and in particular supported 12-molybdophosphoric acid, the selectivity and activity in the partial oxidation are inversely related. It is well known that such a relationship exists for other partial oxidation processes, for example that in which ethylene is converted to ethylene oxide. Since the latter process is operated successfully on a recycling basis, with a relatively low conversion on each pass, it is recommended that the use of a recirculation system, to increase the conversion without sacrificing selectivity, be investigated for heteropoly oxometalates.
10. It is recommended that the effect of changing the design and operation of the catalyst bed be investigated. For example, (a) the oxidation catalyst bed may be operated under a temperature gradient, (b) a tandem bed reactor, consisting of the oxidation catalyst followed (downstream) by a heteropoly oxometalate catalyst capable of converting methanol to hydrocarbons, may be employed. The effect of reactor temperature, relative quantities of the two catalysts and residence time would be investigated in the latter case. The introduction of the tandem bed should convert methanol to C_2-C_6 hydrocarbons before further oxidation of the former can occur.
11. The advantages of the use of a mechanical mixture of the aforementioned oxidation and conversion catalysts should be investigated.
12. The effect of the heat liberation usually encountered in oxidation reactions should also be investigated. Techniques such as the dilution of the catalyst bed with inert material may assist in minimizing the subsequent oxidation of partial oxidation products.

13. It is further recommended that other acidic catalysts be investigated for the partial oxidation of methanol. Since it is well known that the addition of halides, particularly fluorides, to catalysts produces enhanced acidity, such fluorinated catalysts should also be examined. Preliminary work on this aspect has provided encouraging results.

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29. Hayashi, H., and Moffat, J.B., J. Catal. 83, 192 (1983).

30. See, for example, Mizuno, N., Watanabe, T., and Misono, M., J. Phys. Chem. 89, 80 (1985), and references contained therein.

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32. Moffat, J.B., Polyhedron 5, 261 (1986).

33. Taylor, D.B., McMonagle, J.B., and Moffat, J.B., J. Colloid Interface Sci. 108, 278 (1985).

34. McMonagle, J.B., and Moffat, J.B., J. Colloid Interface Sci. 101, 479 (1984).

TABLE 2

Results of the Catalytic Test at 550°C

for the Samples Activated in Stream of Various Gases

Catalyst	Activation in Helium					Activation in Air					Activation in Hydrogen				
		Selectivity Towards:					Selectivity Towards:					Selectivity Towards:			
	Conversion	CO	CO_2	CH_2O	CH_3OH	Conversion	CO	CO_2	CH_2O	CH_3OH	Conversion	CO	CO_2	CH_2O	CH_3OH
HPW_{12}	0.08	51	--	41	8	0.08	26	--	59	15	0.05	36	--	36	28
$HPW_{10}Mo_2$	0.10	20	--	60	20	0.09	75	25	tr	tr	0.11	34	17	44	5
$HPW_{10}V_2$	0.40	88	6	4	1	0.30	54	41	4	1	0.40	70	5	23	2
$HPMo_{12}$	0.77	28	6	37	28	0.64	56	9	25	10	0.75	52	17	30	3
$HPMo_{10}W_2$	0.71	32	6	36	26	0.76	40	5	33	22	0.75	34	5	35	26
$HPMo_{10}V_2$	0.90	78	18	3	1	1.12	75	23	1.0	0.5	0.99	72	23	3	2

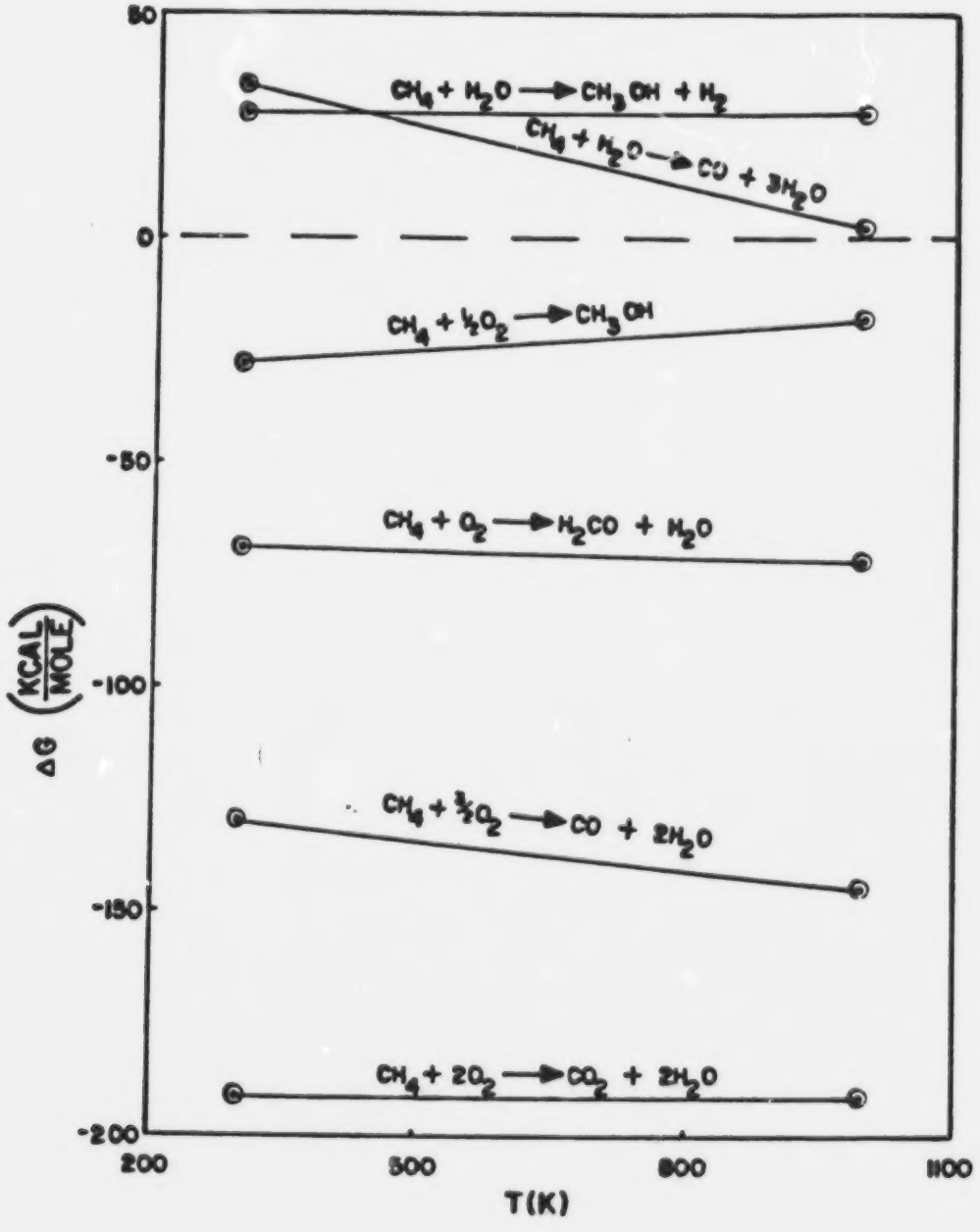
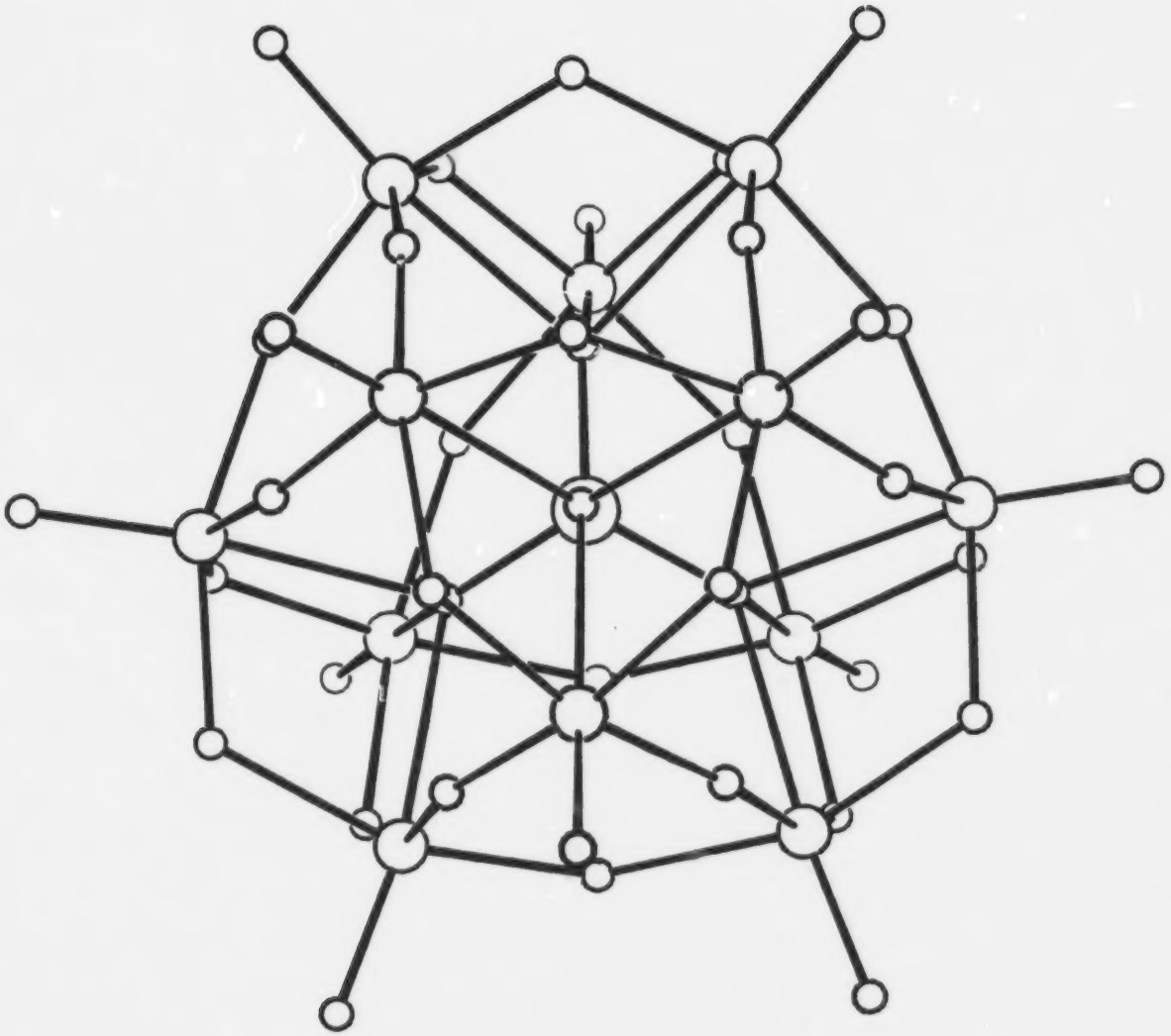

50
0
-50
-100
-150
-200
200
500
800
1100
T(K)
ΔG (KCAL/MOLE)
CH4 + H2O → CH3OH + H2
CH4 + H2O → CO + 3H2O
CH4 + ½O2 → CH3OH
CH4 + O2 → H2CO + H2O
CH4 + 3/2O2 → CO + 2H2O
CH4 + 2O2 → CO2 + 2H2O

Fig. 1



Fig,2

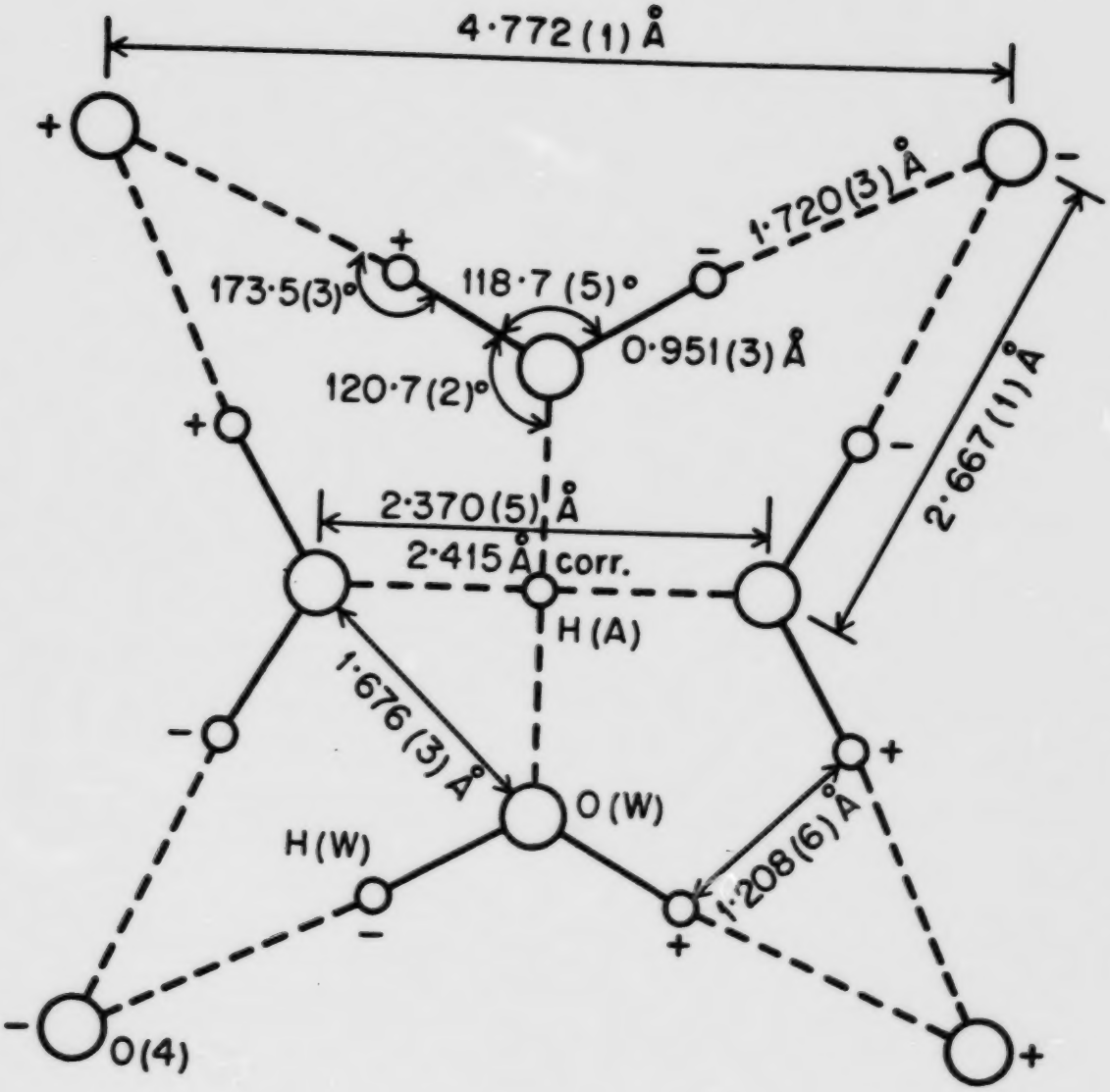

4·772(1) Å
1·720(3) Å
173·5(3)°
118·7(5)°
0·951(3) Å
120·7(2)°
2·667(1) Å
2·370(5) Å
2·415 Å corr.
H(A)
1·676(3) Å
O(W)
H(W)
1·208(6) Å
O(4)

Fig. 3

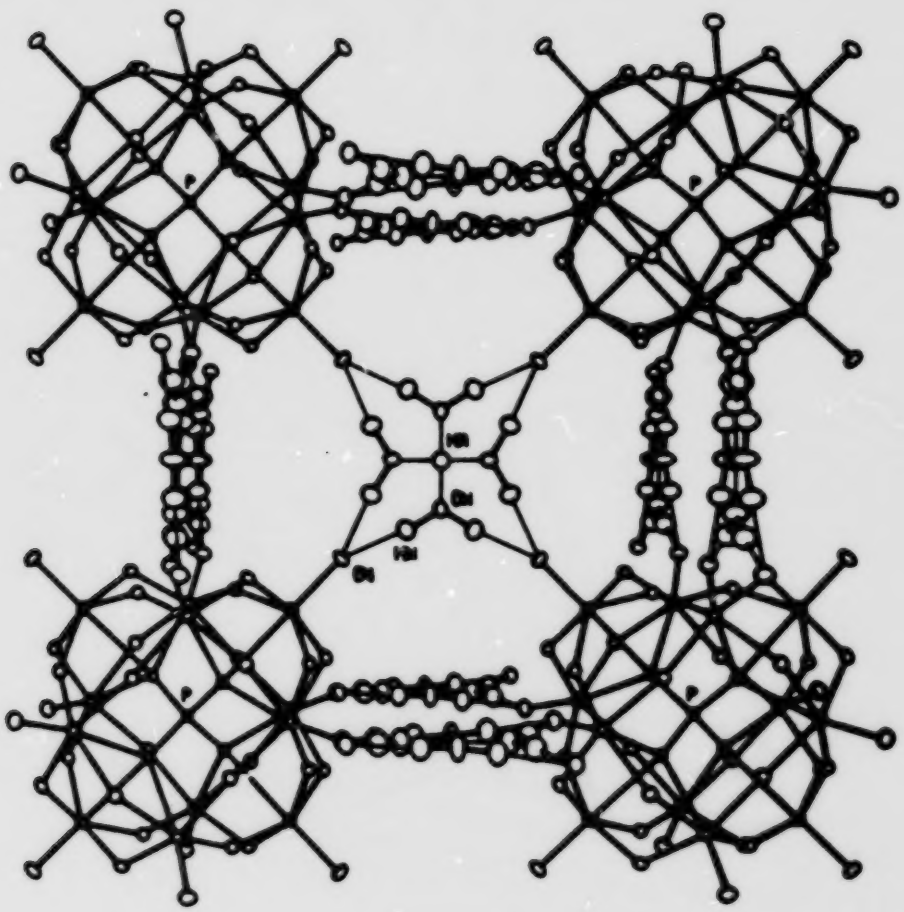


Fig. 4

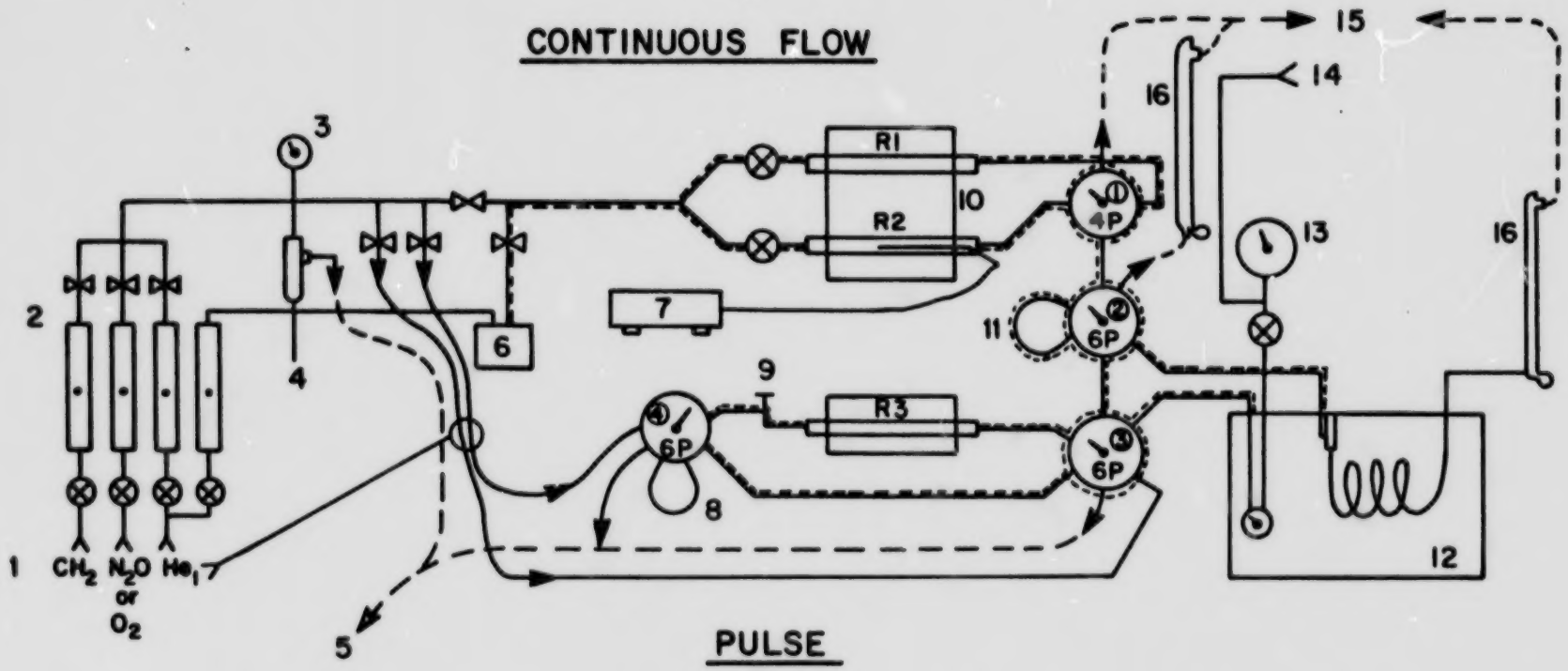


Figure 5: Combined Continuous Flow and Pulse Reactor System

1: gas supplies
2: rotometers
3: pressure gauge
4: pressure relief valve
5: vent 1
6: saturator
7: temperature regulator
8: gas injection valve
9: injection port
10: continuous flow reactors R1 and Rs
11: sampling loop
12: gas chromatograph
13: pressure gauge
14: helium supply to gas chromatograph
15: vent 2
16: bubble flowmeters

Fig.5

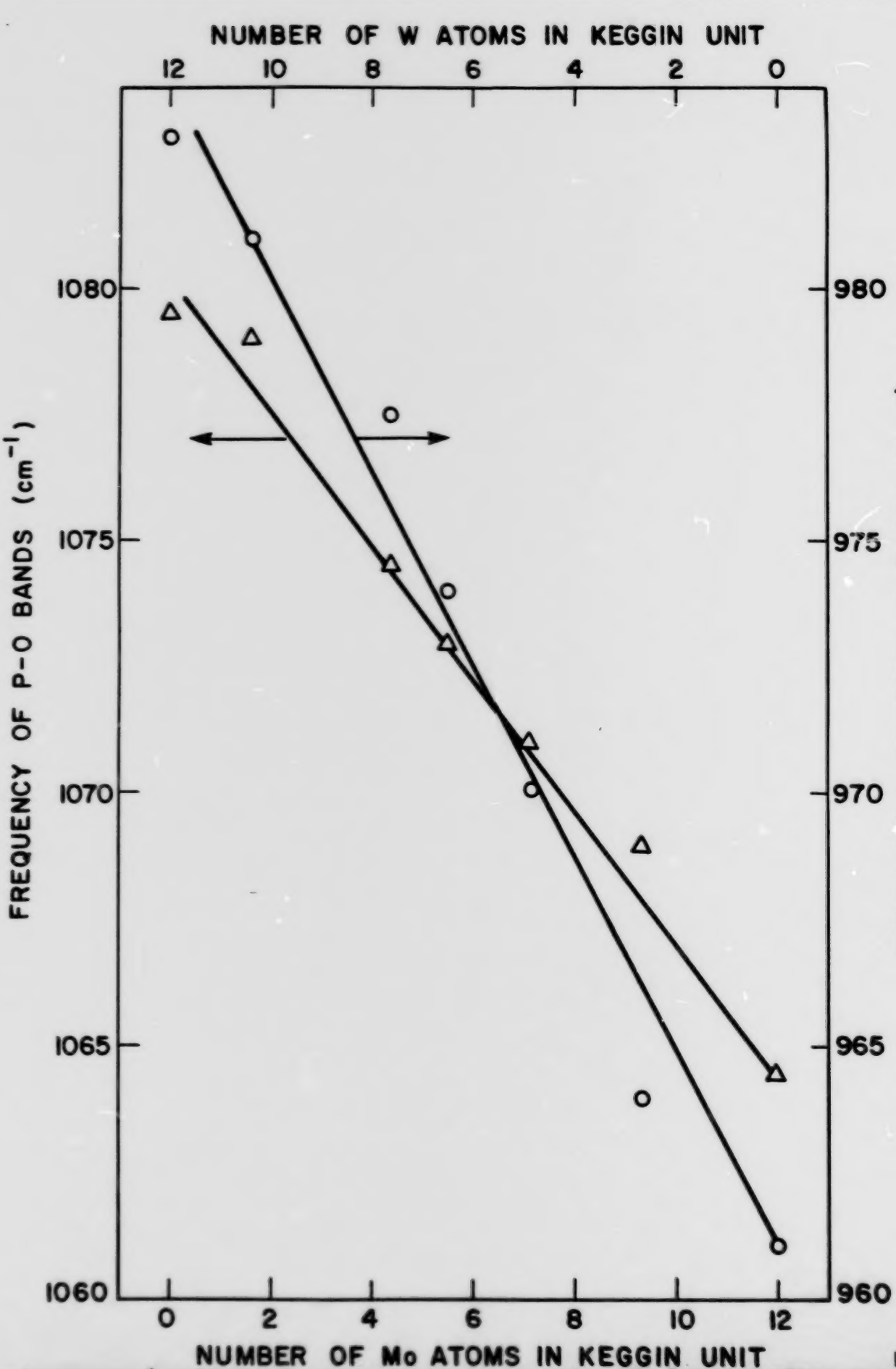

NUMBER OF W ATOMS IN KEGGIN UNIT
12
10
8
6
4
2
0
1080
1075
1070
1065
1060
980
975
970
965
960
FREQUENCY OF P-O BANDS (cm⁻¹)
FREQUENCY OF METAL-O BANDS (cm⁻¹)
0
2
4
6
8
10
12
NUMBER OF Mo ATOMS IN KEGGIN UNIT

Fig. 1

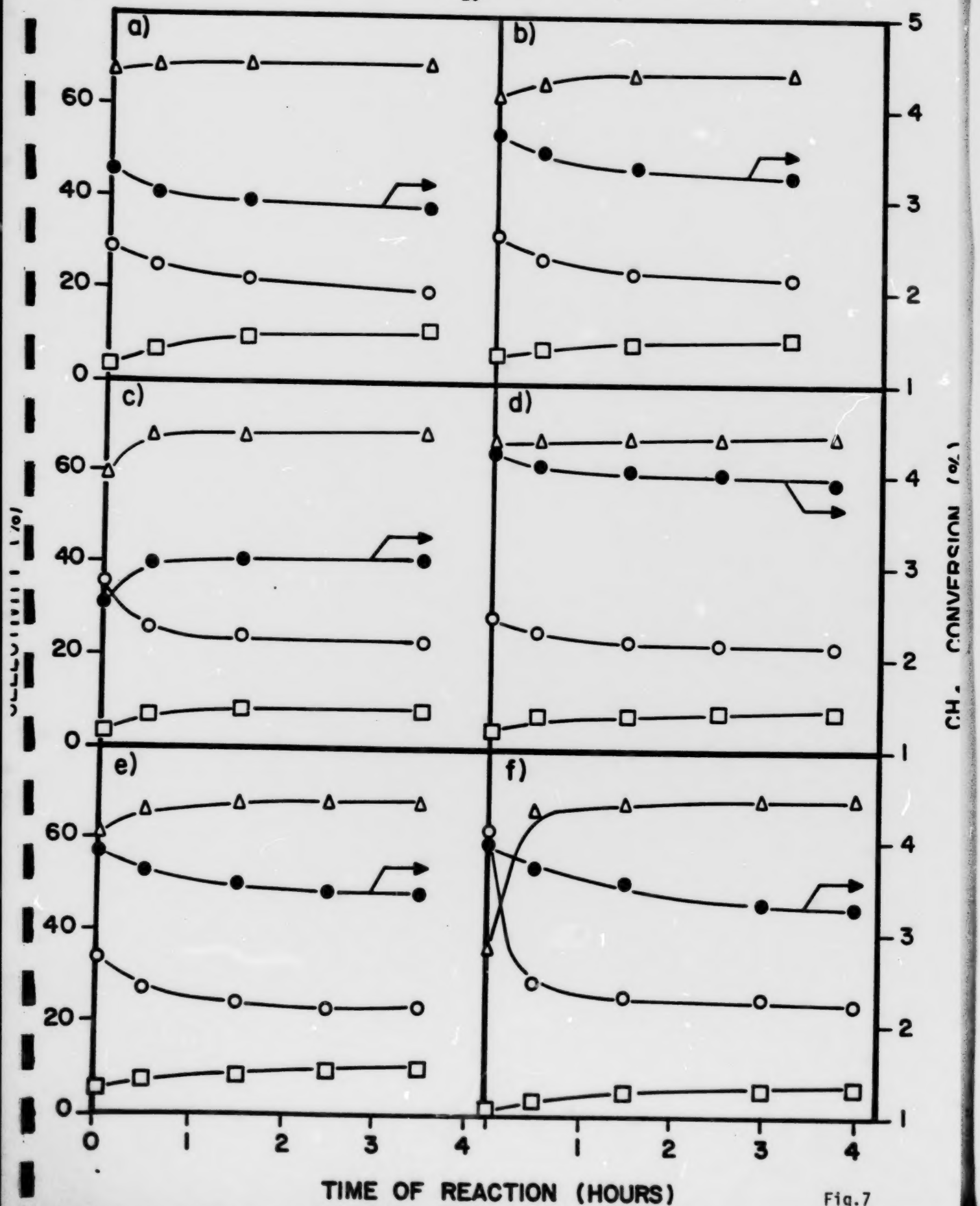

a)
b)
c)
d)
e)
f)
0
20
40
60
1
2
3
4
5
0
1
2
3
4
TIME OF REACTION (HOURS)
CH4 CONVERSION (%)

Fig.7

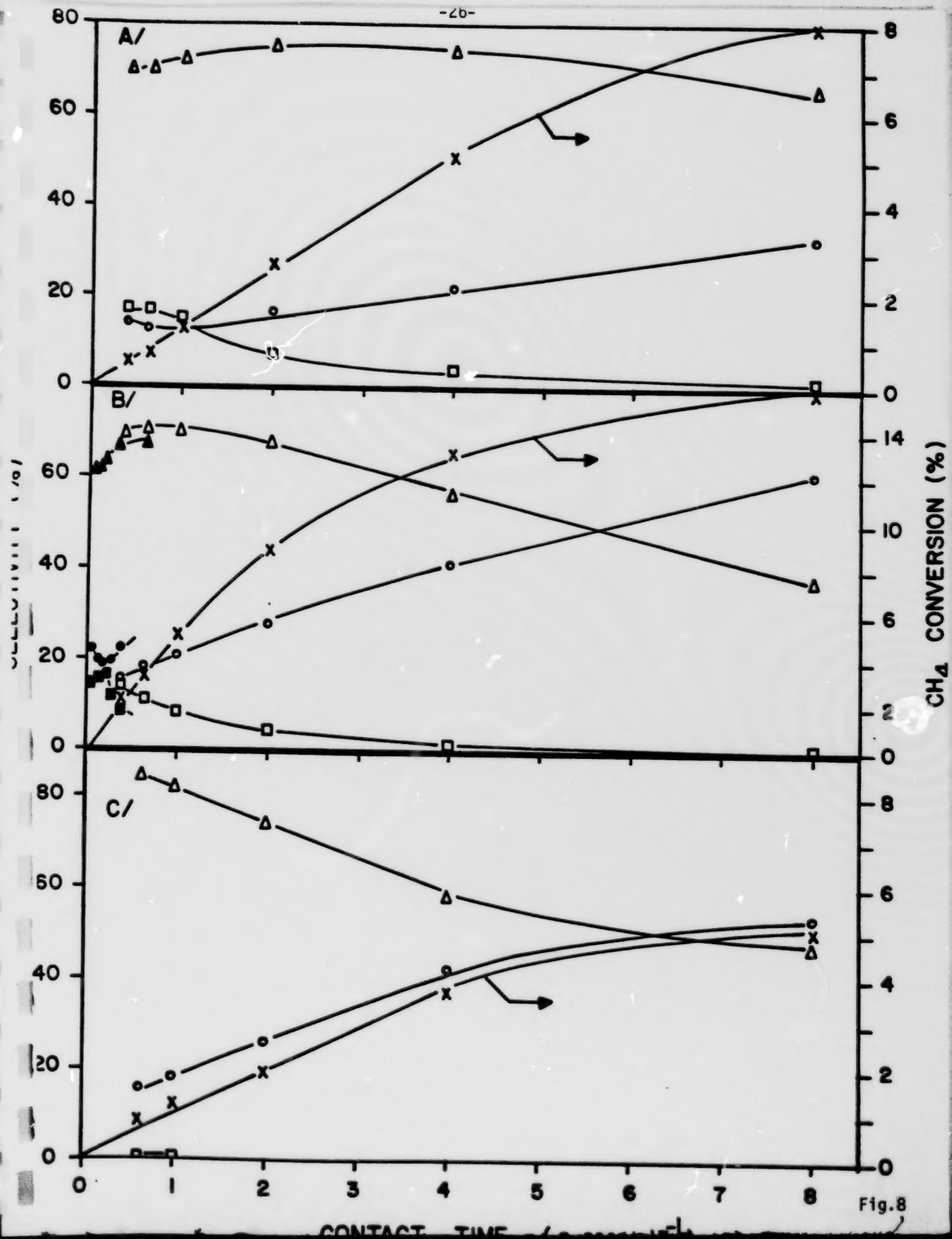

A/
B/
C/
80
60
40
20
0
8
6
4
2
0
14
10
6
2
0
0
1
2
3
4
5
6
7
8
CH4 CONVERSION (%)
CONTACT TIME

Fig.8

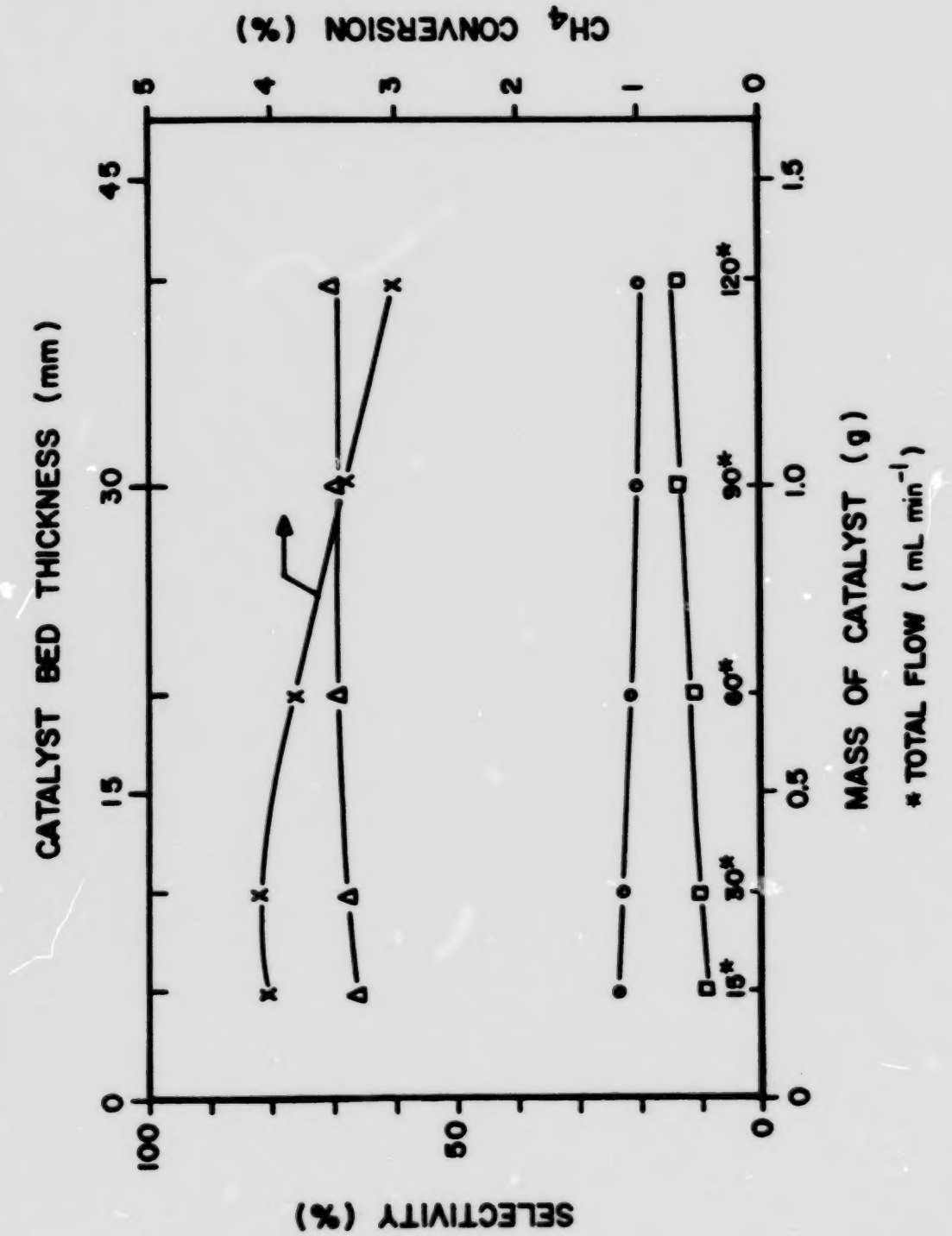

CH4 CONVERSION (%)
CATALYST BED THICKNESS (mm)
SELECTIVITY (%)
MASS OF CATALYST (g)
* TOTAL FLOW (mL min-1)
15*
30*
60*
90*
120*

Fig.9

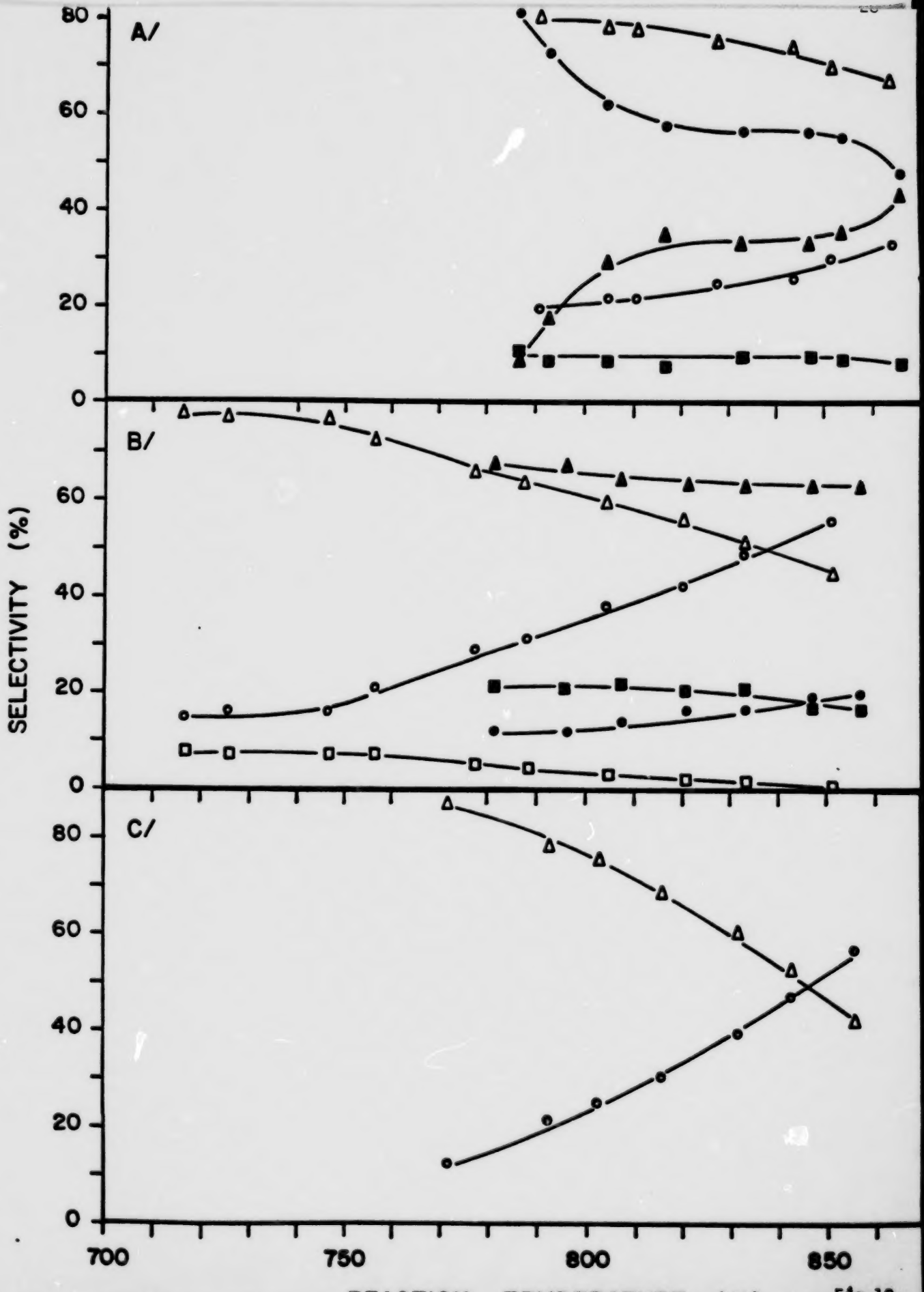
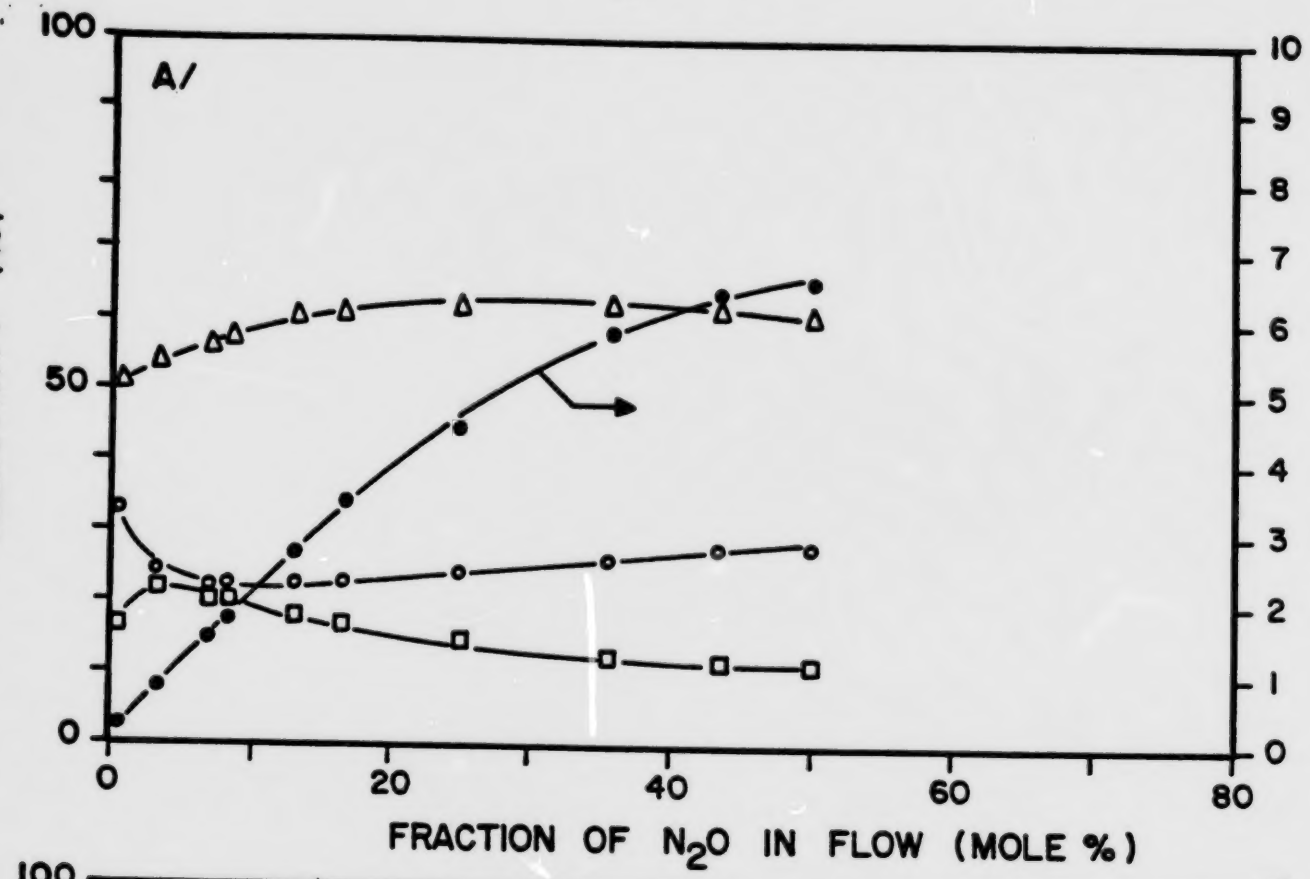

A/
B/
C/
SELECTIVITY (%)
0
20
40
60
80
700
750
800
850
REACTION TEMPERATURE (K)

Fig.10


A/
SELECTIVITY (%)
CH4 CONVERSION (%)
FRACTION OF N2O IN FLOW (MOLE %)
0
20
40
60
80
50
100
10
9
8
7
6
5
4
3
2
1

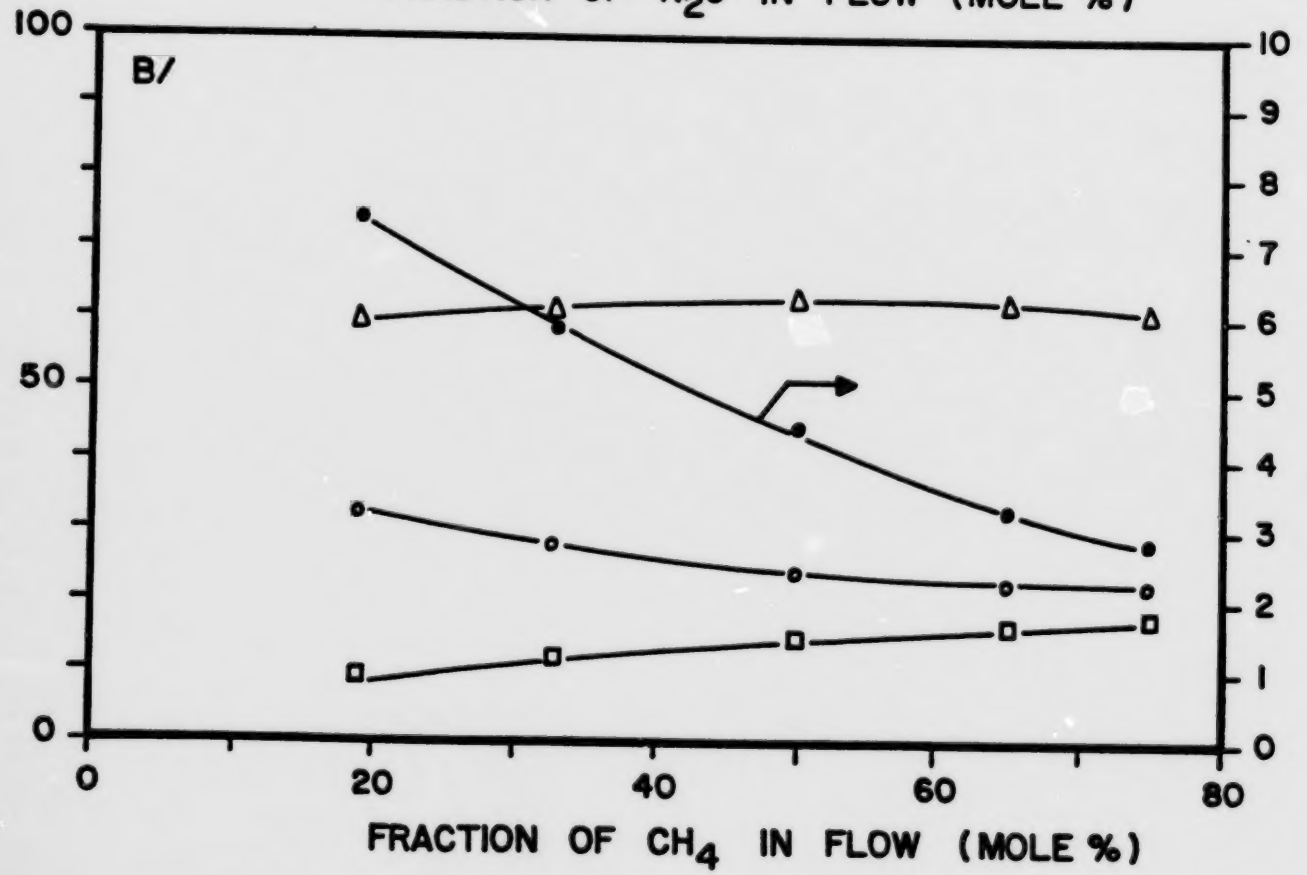

B/
SELECTIVITY (%)
CH4 CONVERSION (%)
FRACTION OF CH4 IN FLOW (MOLE %)
0
20
40
60
80
50
100
10
9
8
7
6
5
4
3
2
1

Fig.11

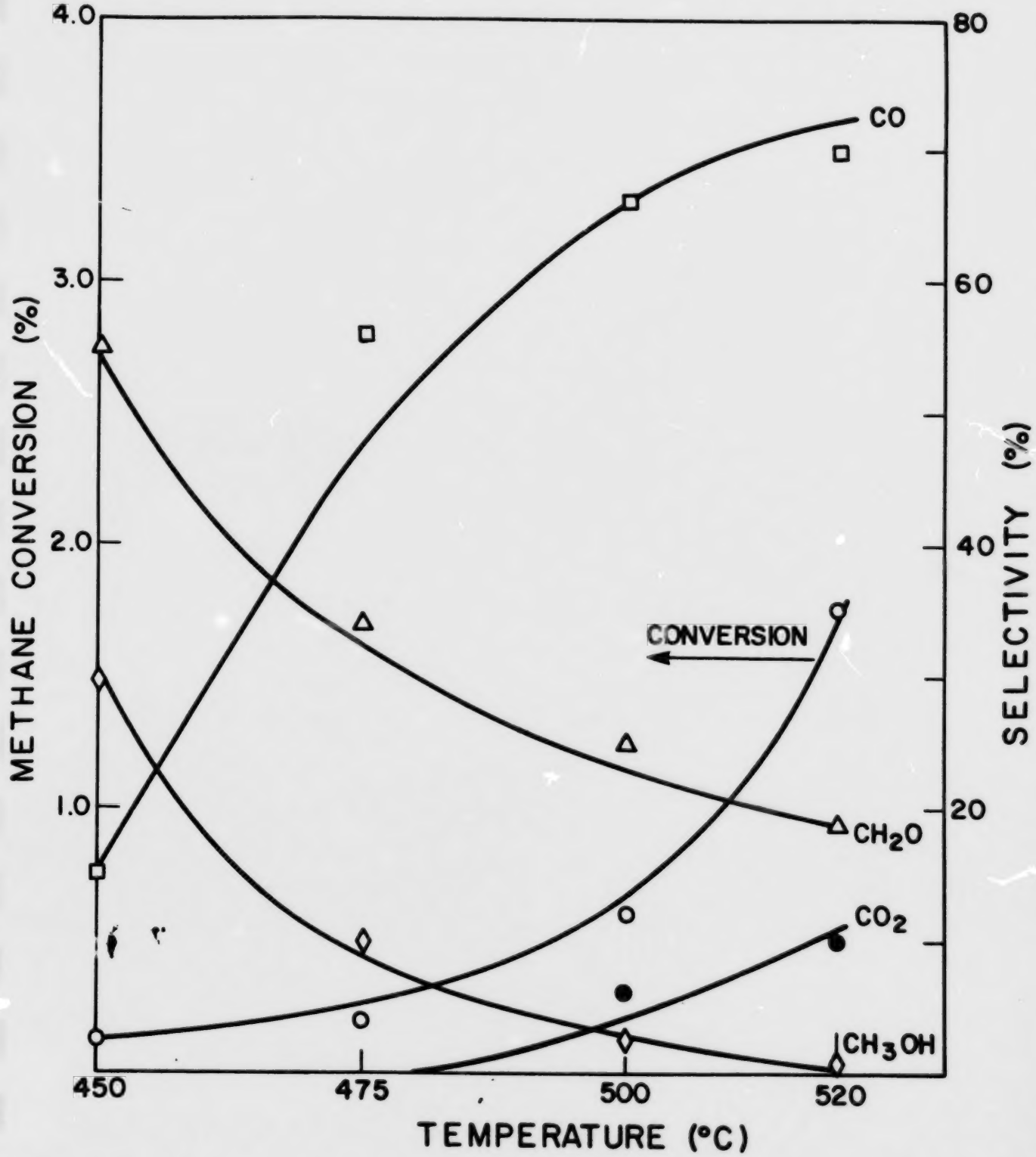

4.0
3.0
2.0
1.0
80
60
40
20
METHANE CONVERSION (%)
SELECTIVITY (%)
CO
CONVERSION
CH_2O
CO_2
CH_3OH
450
475
500
520
TEMPERATURE (°C)

Fig.12

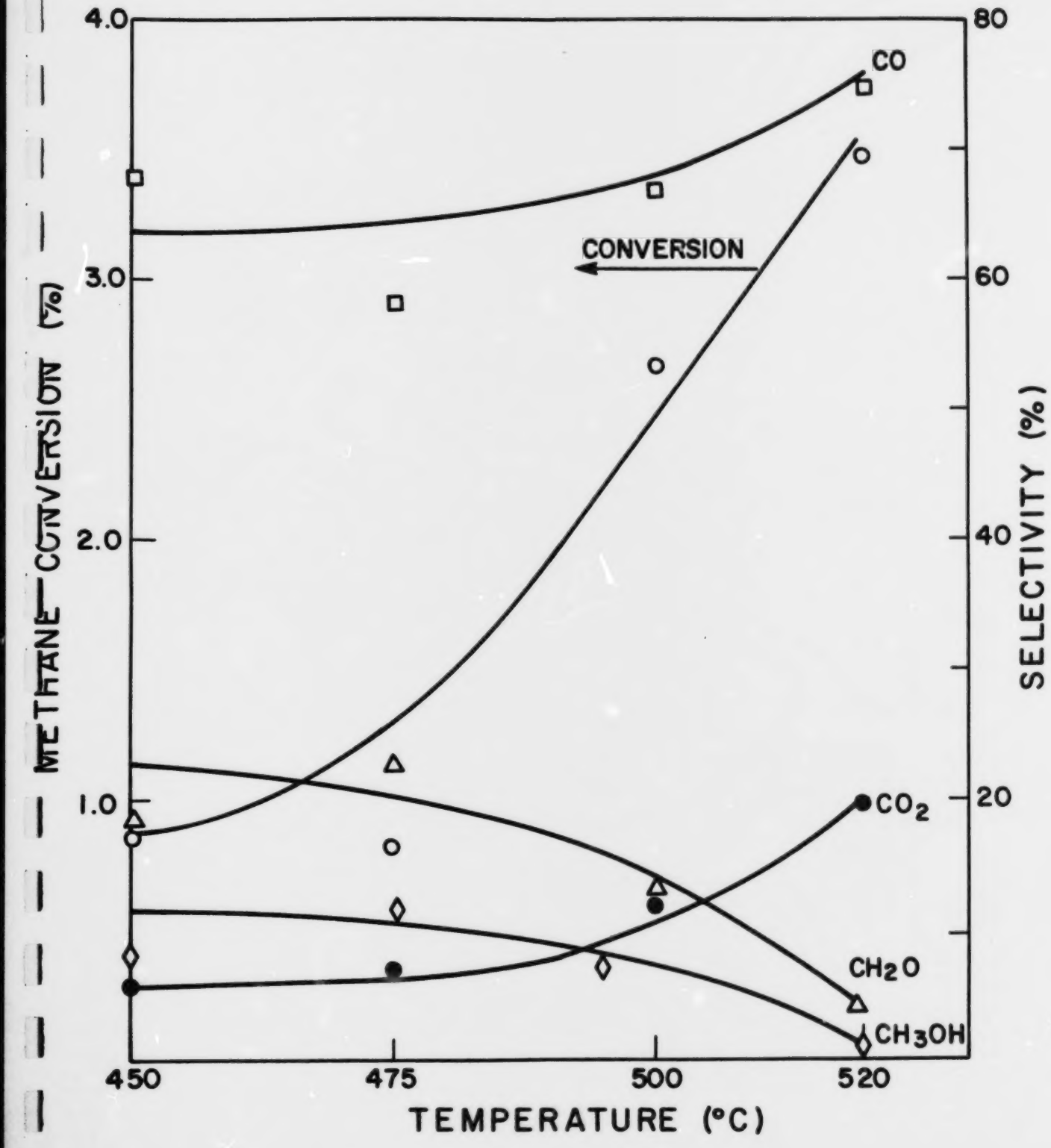

4.0
3.0
2.0
1.0
80
60
40
20
CO
CONVERSION
CO_2
CH_2O
CH_3OH
METHANE CONVERSION (%)
SELECTIVITY (%)
450
475
500
520
TEMPERATURE (°C)

Fig.13

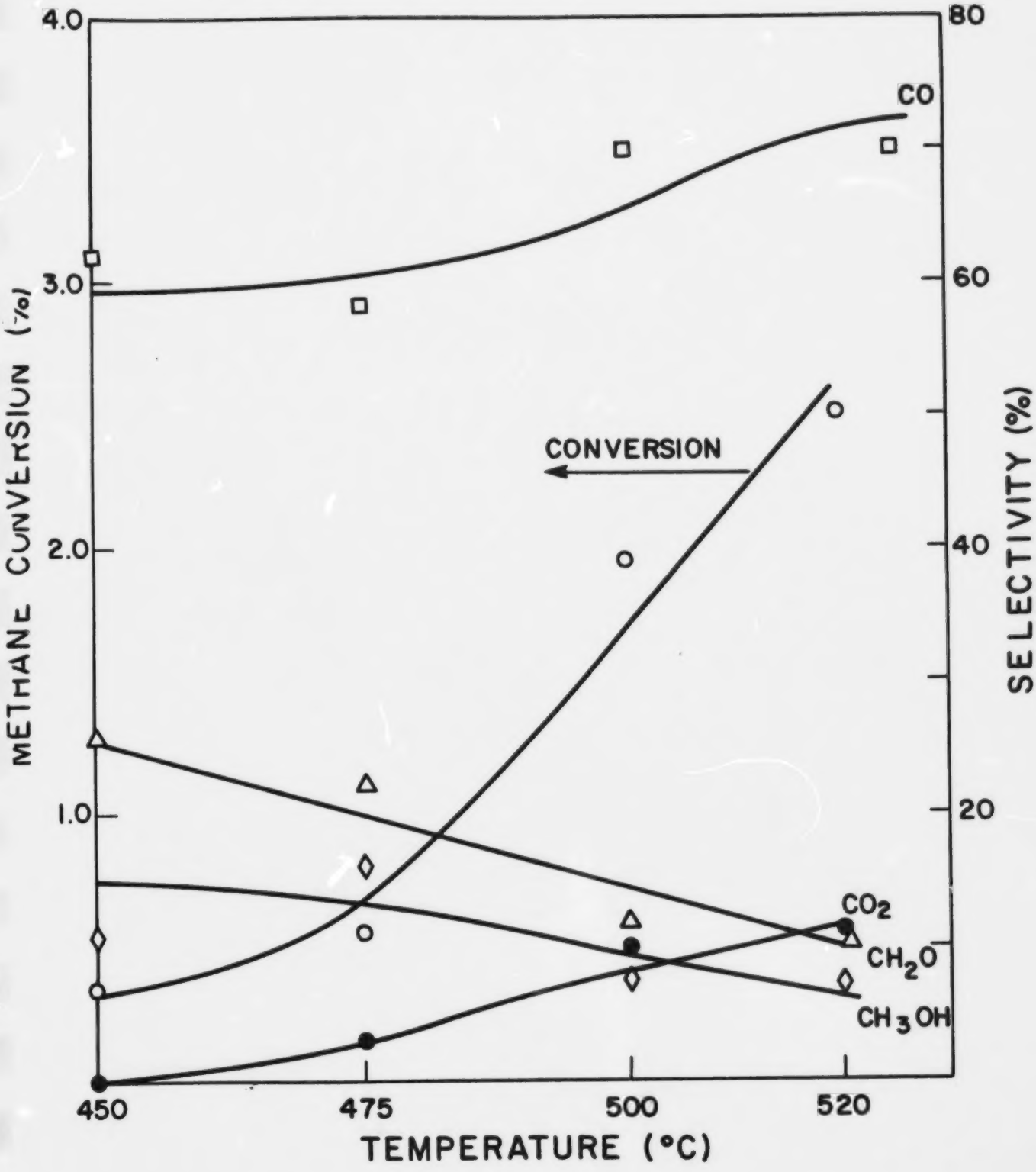

4.0
3.0
2.0
1.0
80
60
40
20
CO
CONVERSION
CO_2
CH_2O
CH_3OH
METHANE CONVERSION (%)
SELECTIVITY (%)
450
475
500
520
TEMPERATURE (°C)

Fig.14

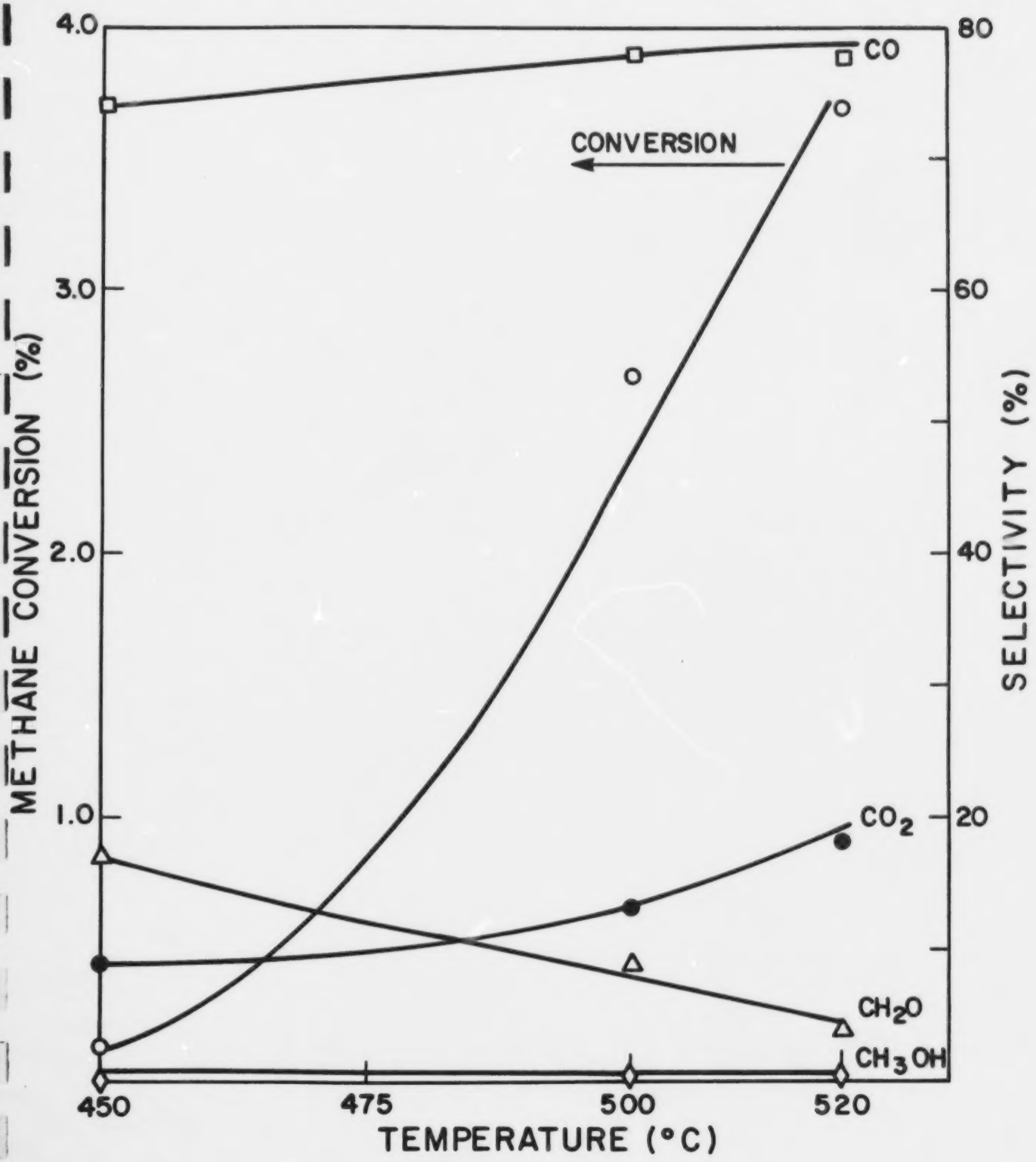

4.0
3.0
2.0
1.0
80
60
40
20
CO
CONVERSION
CO_2
CH_2O
CH_3OH
450
475
500
520
METHANE CONVERSION (%)
SELECTIVITY (%)
TEMPERATURE (°C)

Fig.15

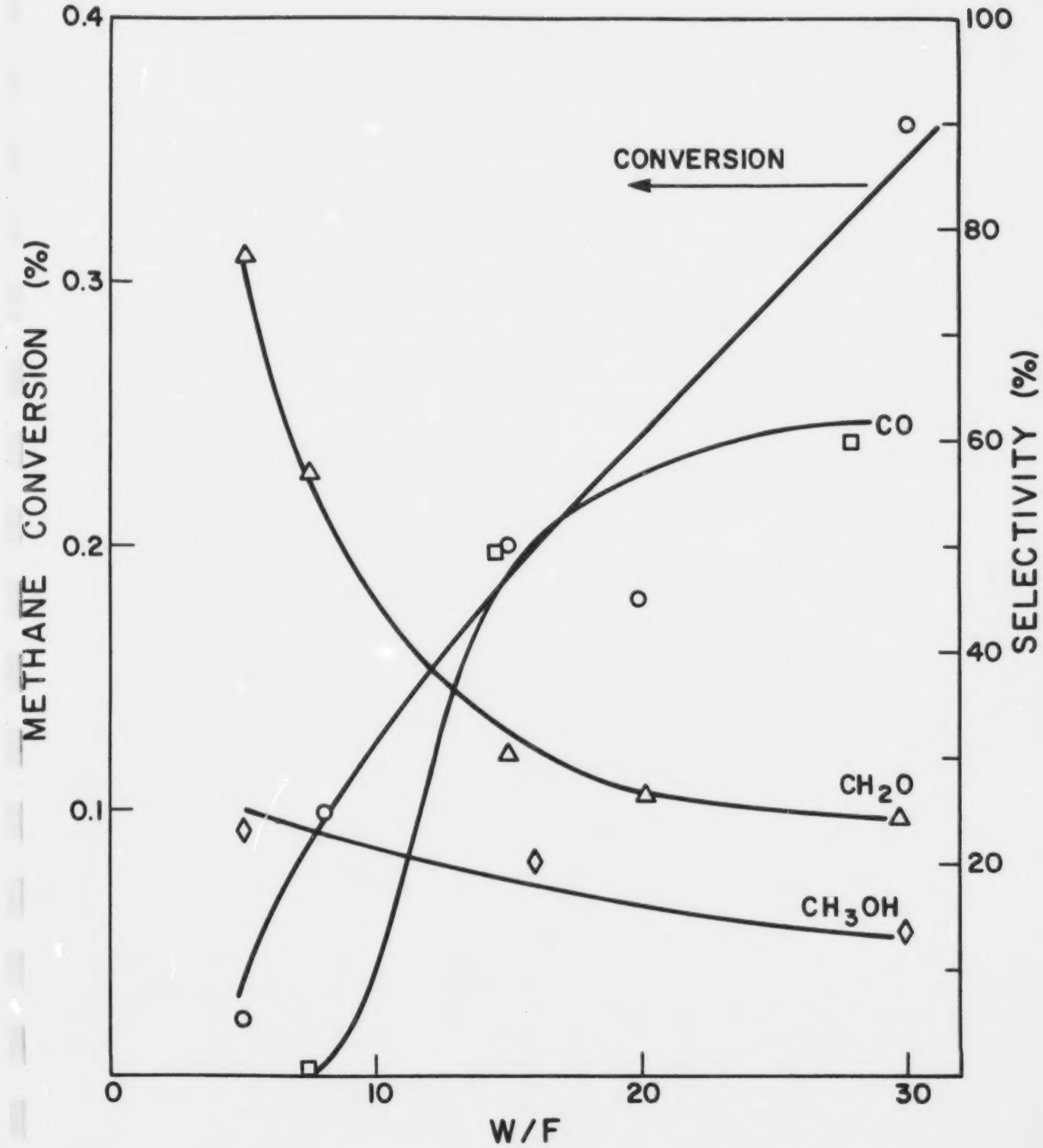

0.4
0.3
0.2
0.1
0
10
20
30
100
80
60
40
20
CONVERSION
CO
CH_2O
CH_3OH
METHANE CONVERSION (%)
SELECTIVITY (%)
W/F

Fig.16

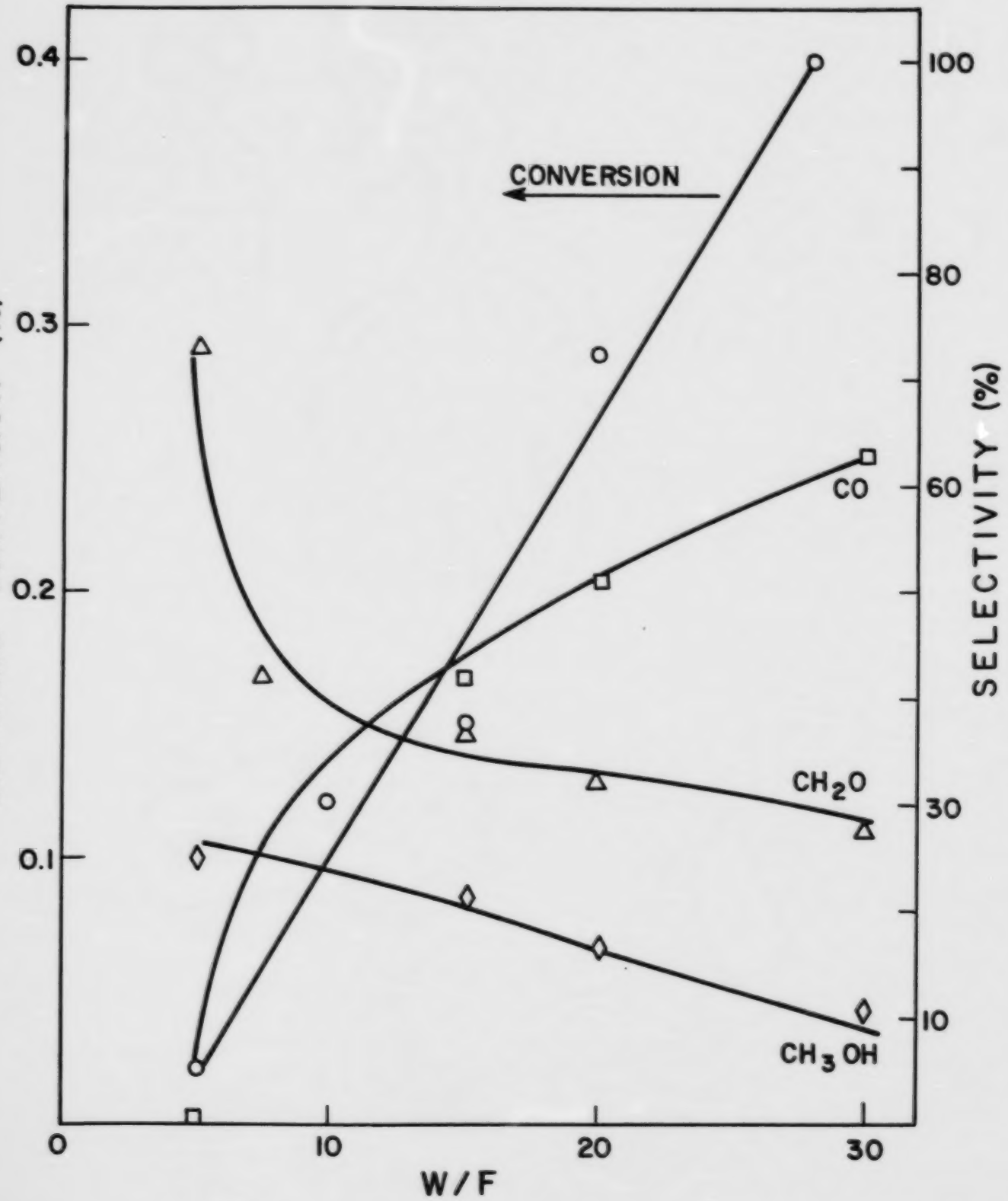

METHANE CONVERSION (%)
SELECTIVITY (%)
W/F
CONVERSION
CO
CH_2O
CH_3OH
0.4
0.3
0.2
0.1
0
10
20
30
100
80
60
30
10

Fig.17

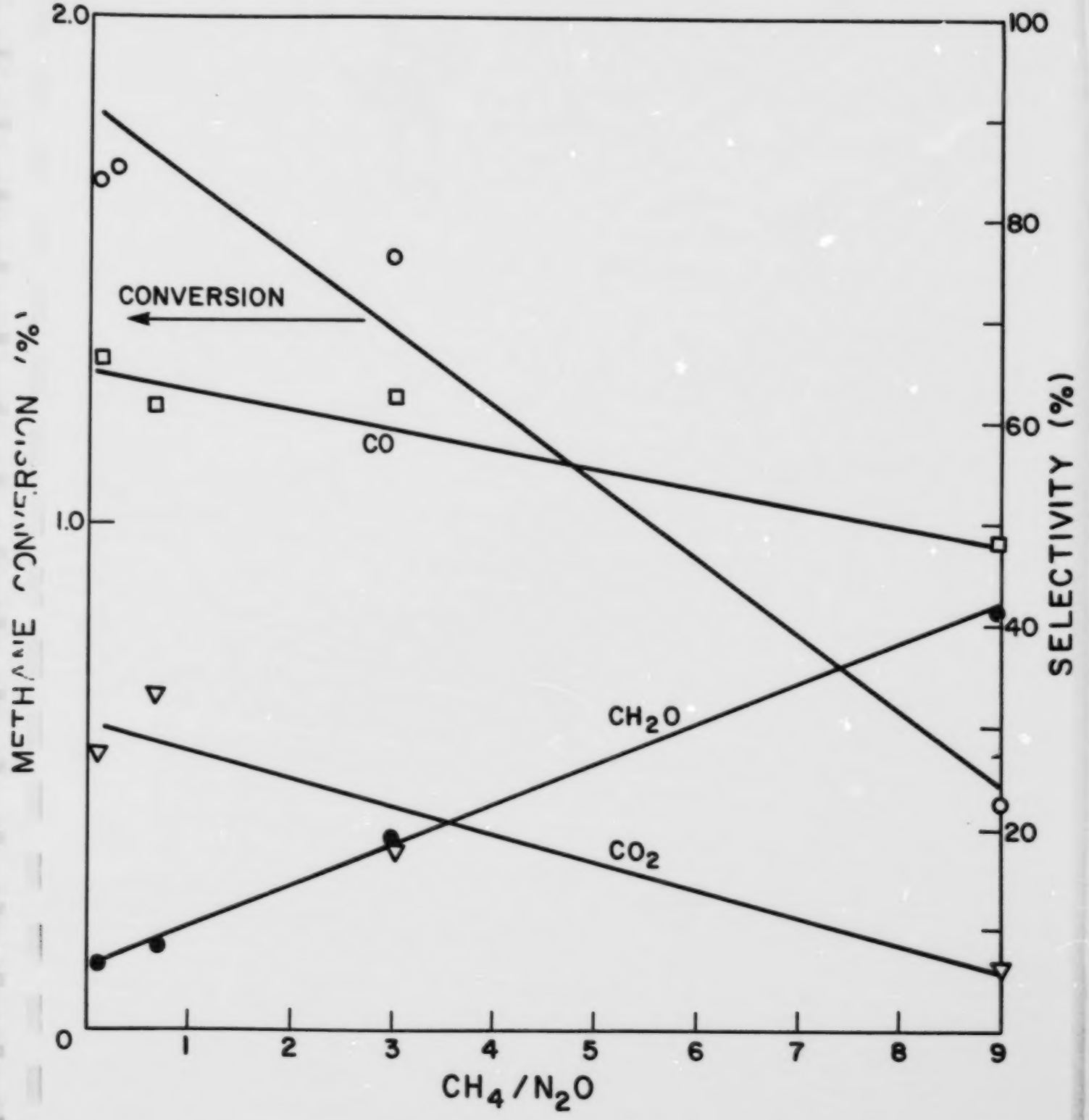

2.0
1.0
0
METHANE CONVERSION (%)
100
80
60
40
20
SELECTIVITY (%)
CONVERSION
CO
CH_2O
CO_2
1
2
3
4
5
6
7
8
9
CH_4 / N_2O

Fig.18

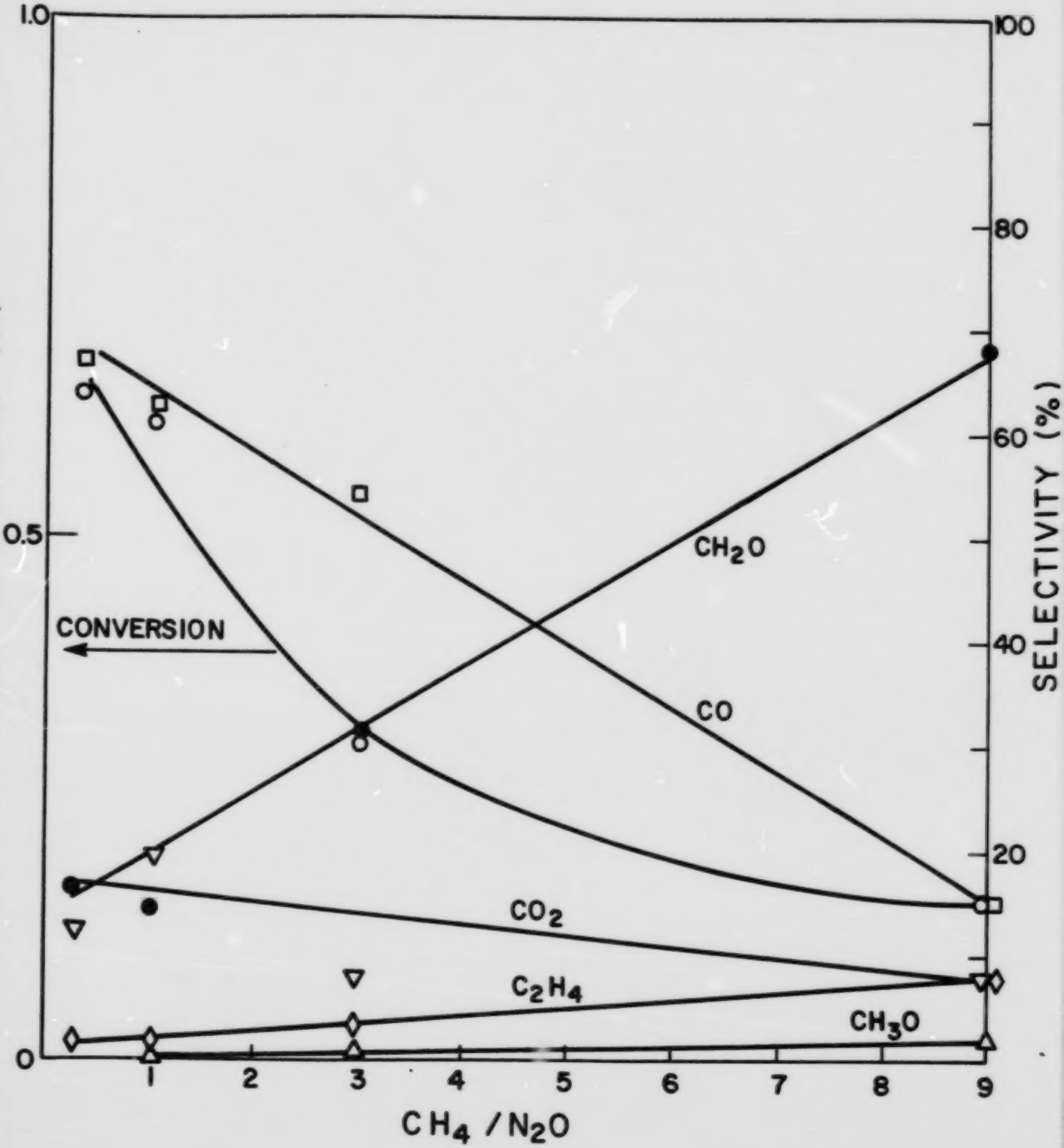

1.0
0.5
0
100
80
60
40
20
METHANE CONVERSION (%)
SELECTIVITY (%)
CONVERSION
CH2O
CO
CO2
C2H4
CH3O
1
2
3
4
5
6
7
8
9
CH4 / N2O

Fig. 19

APPENDICES

(a) Catalytic Properties of Silica-Supported Heteropoly Acids.

(b) Nature and Stability of the Supported Species.

(c) Effect of Addition of Cesium on Silica-Supported 12-molybdophosphoric Acid, Molybdena, Vanadia and Iron Oxide.

(d) Properties of the Silica-Supported Salts of 12-molybdophosphoric Acid.

THE OXIDATION OF METHANE ON HETEROPOLYOXOMETALATES

I. CATALYTIC PROPERTIES OF SILICA-SUPPORTED HETEROPOLYACIDS

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ABSTRACT

The catalytic properties in the partial oxidation of methane of a number of silica-supported heteropoly acids, 12-tungstophosphoric, 12-molybdophosphoric, 10-molybdo-2-vanadophosphoric, 12-tungstosilicic, and 12-molybdosilicic acids have been investigated. The highest activity and selectivity were found with 12-molybdophosphoric acid on SiO_2 with N_2O as oxidant, although a catalyst prepared from ammonium vanadate/SiO_2 showed a higher conversion of methane. The effect of pretreatment environment, reactivity of the products, deactivation of the catalyst and reaction parameters have also been studied.

INTRODUCTION

The current interest in the oxidation of methane arises from two sources - the inherent practical advantages of a liquid as compared to a gaseous fuel and the scientifically intriguing problem of carbon-hydrogen bond activation. In the last several years a number of publications concerning the heterogeneously catalyzed oxidation of methane have appeared (2-15) and most recently two reviews have been published (16-17).

Gas phase studies by Bohme and Fehsenfeld (1) showed that the O^- ion was capable of stripping a hydrogen atom from an alkane.

$$O^- + RH \rightarrow OH^- + R \qquad (1)$$

Subsequently, Lunsford and coworkers (2,3) have shown that low molecular weight alkanes can be partially oxidized at room temperature over MgO with N_2O, apparently as a result of the abstraction of a hydrogen atom by O^-, followed by the reaction of alkyl radicals with surface O^{2-} ions. The formation of methyl radicals from the reaction of surface O^- with methane on molybdenum supported on silica has also been shown by Lipatkina et al (4).

In further work, Lunsford et al (5-9) have studied the catalytic oxidation of methane and ethane over Mo/SiO_2 catalyst, with N_2O as an oxidant, and most recently (10) have shown that conversion of methane to ethylene and ethane can be achieved with O_2 as the oxidant over a lithium-promoted magnesium oxide catalyst.

The kinetics of the partial oxidation of methane with N_2O over a molybdena-silica catalyst have recently been studied by Somorjai et al (11). These workers find that water vapour is required at low temperatures, where parallel processes lead to methanol and formaldehyde from the same intermediate, while at higher temperatures formaldehyde is formed from methanol.

It has recently been shown (12) that the gas-phase radical formation during the reactions of methane, ethane, ethylene, and propylene over various oxide catalysts is dependent on the bond strength of the weakest C-H bond, the presence of particular radical-forming sites on the catalyst surface, and the ability of the radicals to desorb or take part in further surface reactions. The influence of experimental conditions on the formation of O^- ions from N_2O adsorption on reduced grafted Mo/SiO_2 and the role of these ions in surface charge-transfer reactions has also been analyzed recently (13-14).

Although considerable attention has been focussed on Mo/SiO_2 as a catalyst for the partial oxidation of methane, V/SiO_2 has recently been shown to be both active and selective for this process (15).

In this laboratory the structural, surface, and heterogeneous catalytic properties of heteropolyoxometalates have recently been studied by a variety of techniques (18-21). This work has concentrated on those heteropoly compounds with Keggin structure. These are ionic solids in which the anion has a high molecular weight, cagelike structure, with an atom such as phosphorus, silicon, or arsenic at its centre and four oxygen atoms tetrahedrally arranged around the central atom. Twelve octahedra, with an oxygen atom at each of the vertices and a metal atom such as molybdenum, tungsten, or vanadium, at each of their centres, surround the central tetrahedron and share oxygen atoms with each other and the former.

In particular it has been shown by temperature-programmed-desorption, -reduction, and -exchange experiments (18-20) that water is desorbed at two temperatures, that at the higher temperature resulting from the abstraction of oxygen from the heteropoly anion by the acidic protons. Further, photoacoustic FTIR studies (20,21) have shown that the dehydration of methanol on

12-tungstophosphoric acid involves the methylation of anionic (presumably terminal) oxygen atoms. Extended Huckel calculations (22) have shown that the acid strength of the protons in the heteropoly acids is inversely related to the charge on these terminal oxygen atoms, while the catalytic activity in oxidation processes appears to be proportional to the strength of the anionic peripheral metal-oxygen bond.

Earlier work from this laboratory has shown that 12-tungstophosphoric acid (23,24) and its metal and ammonium salts (24-26) are capable of converting methanol to hydrocarbons ($>C_1$) presumably via a route in which the anionic terminal oxygen atoms are methylated. In contrast, with 12-molybdophosphoric acid, methanol is primarily converted to oxidation products, principally carbon monoxide. In the former case higher reaction temperatures, for example, those greater than 400°C produce a reaction product which is predominantly methane, rather than higher hydrocarbons. It thus appeared possible that the methylation of the terminal anionic oxygen atom may be achieved by the use of methane as reactant rather than methanol.

A number of other workers (27) have shown that certain heteropolyoxometalates are effective in oxidation processes, although no work has yet been published relating to the oxidation of methane.

In the present work the first report of the partial oxidation of methane on the heteropolyoxometalates, 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiMo), 12-tungstophosphoric (HPW), 12-tungstosilicic (HSiW), and 10-molybdo-2-vanadophosphoric ($HPMo_{10}V_2$) acids is presented. Emphasis has been placed on the effect of reaction variables and on the comparison of N_2O and O_2 as oxidant on the catalytic properties of 12-molybdophosphoric acid supported on SiO_2.

EXPERIMENTAL SECTION

Catalyst Preparation. A silica gel (Grace-Davison grade 400, 740 ± 20 m^2g^{-1}) with particle size of 8-20 mesh has been used as a support. The supported heteropolyoxometalates have been prepared by impregnation of the silica with aqueous solutions of HPMo (B.D.H. Analar grade), HSiMo (Pressure Chemical Co.), HPW (B.D.H. Analar grade), HSiW (J.T. Baker Analysed) and $HPMo_{10}V_2$ prepared following the procedure reported by Tsigdinos (28). The acids were purified by recrystallization in distilled water prior to use. Ten grams of support were impregnated with 20 mL of solution of the acid at its natural pH (≈2-3). The solutions were then evaporated to dryness at 80°C and the solids calcined at 350°C for 2 hours. The samples were then sieved and the 8-15 mesh particle size kept for use.

Samples containing 3 wt% molybdenum and 1.66 wt% vanadium on silica have also been prepared following the method used by Liu et al. (8). A large excess of basic solution (pH = 11 by NH_4OH addition) of ammonium molybdate (J.T. Baker Analysed) or ammonium vanadate (Fisher-purified) was added to the support, then evaporated at 80°C to dryness. The Mo/SiO_2 catalyst has been calcined at 600°C for 16 hours and the V/SiO_2 catalyst at 350°C for 2 hours.

The samples will be symbolised in the text by the wt% of the acids followed by the abbreviation HPMo, HSiMo, HPW, HSiW, HPV_2Mo_{10} for $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ and the wt% of the metal followed by Mo or V for supported molybdenum and vanadium, respectively.

The loading of a set of different supported heteropolyoxometalates has been chosen in order to obtain a similar surface concentration of heteropolyanionic unit, the Keggin Unit (KU), of 0.087 KU per nm^2 of support surface area. This corresponds to loadings of 20.0, 19.9, 26.2, 26.2 and 20.4 wt% of the HPMo, HSiMo, HPW, HSiW and HPV^2Mo^{10}, 30 H^2O hydrated acids respectively. A 29.4 wt%

HSiMo, HPW, HSiW and HPV_2Mo_{10}, 30 H_2O hydrated acids respectively. A 29.4 wt% HPMo on SiO_2 has also been prepared.

A sample of the silica support was impregnated with an acidic aqueous solution (HNO_3, pH=2), then dried and calcined at 350°C for 2 hours in order to simulate the effect of the impregnation of the heteropolyacids. This sample has been used as the support reference catalyst.

Catalytic experiments. The catalytic tests have been performed in a fixed-bed continuous flow reactor. The flow of reactant was regulated by needle valves and monitored by rotameters. All the gases, He (99.9%), CH_4 (99.0%), N_2O (99.0%), O_2 (99.0%), CO (99.0%) were used without further purification. The H_2O, CH_3OH or CH_2O vapor were generated by a saturator under helium when necessary.

The pyrex glass or quartz reactor measured 33 cm in length and 0.9 cm in diameter (o.d.). The catalyst bed was supported between pads of pyrex glass wool of 5 cm thickness. The temperature was monitored by a thermocouple located in the catalyst bed. Temperature variations were found to be in the range ±1°C along the central part of the reactor (≈8 cm). The reaction manifold was constructed from stainless steel 1/8 inch o.d. and heated at 150°C. A 6-port gas sampling valve (VALCO) with a 5 mL sample loop was connected to the reactor exit and to a reactor by-pass. This permitted the analysis of both the reactor inlet and outlet flow.

The samples were preheated in He, unless otherwise reported, for one hour at the reaction temperature. This produced extensively dehydrated samples as only traces of water were then detected by GC analysis.

All the products were analysed with a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector and with a Porapak Q column of 5.5 meter length and helium as a carrier gas (Flow : 60 mLmin^{-1}, Column

pressure 60 psi). The temperature program of 4 minutes at 35°C, ramp of 25°C min^{-1} to 120°C, 10 minutes at 120°C, ramp of 10°C min^{-1} to 200°C gave satisfactory separation of all gases except N_2-O_2. The presence of these gases was checked with a 3A molecular sieve column when necessary. The calibrations have been made for each component in actual analysis condition. When N_2O is used as oxidant a mass balance of N better than 98% was usually found. Carbon and oxygen mass balances are generally better than 95% when the conversion is higher than 1% but is always better than 90%. The imprecision arises in part because of the coking of the samples and a lower precision in the detection of small amounts of CO, CO_2, CH_2O and CH_3OH.

The steady state was reached after several hours of reaction. The conversion of CH_4 was calculated as: 100X (amount of C product detected/amount of CH_4 in the inlet flow). The conversion of N_2O was calculated from the N_2 produced and conversion of O_2 from the oxygenated products formed.

The selectivity was calculated as the mol% of the CO, CO_2, CH_2O and CH_3OH product formed. Traces of C_2H_6, C_2H_4 and other hydrocarbons and dimethylether have been omitted from the calculation.

Blank runs have been performed with the reactor full of glass wool heated at 570°C with conditions similar to those employed when a catalyst was present. In helium, CH_4 and CO produced no decomposition or reaction products whereas N_2O yielded traces of N_2 and O_2, CH_3OH formed traces of dimethylether and CH_2O gave large traces of CO, H_2, CH_3OH and H_2O. In the presence of N_2O or O_2, CH_3OH, CH_2O and CO each produced traces of CO, CO_2 and H_2O whereas CH_4 gave no detectable products.

Activation energies have been calculated from 4 to 6 runs at different temperatures, recorded in random order when the system was in steady state.

RESULTS

Catalytic properties of the supported heteropolyoxometalates.

The conversion and selectivity of the different supported heteropolyoxometalates and comparison catalysts are reported in Table 1 together with the N_2 production turnover rate per Keggin Unit (KU) or atom of metal when nitrous oxide is used as the oxidant (Table 1a).

With nitrous oxide as oxidant the conversion of methane on the silica support is small and only complete oxidation products are produced. The conversion of methane on supported tungsten based KU remains small, whereas molybdenum containing KU are much more active. Moreover these two categories of catalysts show distinct differences in selectivity, the partial oxidation products, namely formaldehyde and methanol being produced mainly by the molybdenum containing KU, while only traces of formaldehyde were produced by the HPW and HSiW catalysts. These results show that the nature of the peripheral metal atom of the Keggin Unit structure is important. The introduction of two vanadium atoms in the Keggin structure to yield $H_5PV_2Mo_{10}O_{40}$ produces little change compared to the HPMo catalysts, the conversion being slightly lower and the selectivity being similar.

The effect of the nature of the central heteroatom P or Si, can also be estimated from the results of Table 1. Both for Mo- or W- containing KU the change of the central heteroatom from phosphorus to silicon produces a decrease of the catalytic activity and a change of selectivity, the silicon central heteroatom favoring the production of CO_2 at the expense of CO with only a slight decrease of the selectivity of formaldehyde and methanol relative to the KU containing phosphorus as the central atom.

Although the loadings are slightly different, a comparison of the N_2 production turnover rate per metal atom of the different heteropolyoxometalates and the supported Mo and V catalysts can be made. The supported HPMo, HPV_2Mo_{10} and HSiMo gave a turnover somewhat higher than the Mo catalyst whereas the V catalyst is clearly much more active. The selectivity of the Mo and HSiMo catalyst are surprisingly similar whereas the V catalyst has a very different selectivity with a higher CO production, less CO_2 and CH_2O but still with some CH_3OH produced. A net difference of the ratio of CH_2O/CH_3OH produced can also be found between the V and the other catalysts.

When oxygen is used as the oxidant, (Table 1b), the silica support shows a surprisingly good selectivity toward the production of formaldehyde with a small conversion. The conversion of the HPMo catalyst remains small with now a very poor selectivity to partial oxidation products. On that catalyst, for rather similar experimental conditions, the use of oxygen give a much smaller methane conversion than that obtained with nitrous oxide as oxidant.

These results show that the supported 12-molybdophosphoric acid is the most active and selective catalyst of the supported heteropolyoxometalates examined in the present work. This system has therefore been choosen for a more detailed study.

Pretreatment and deactivation. A helium pretreatment of the catalyst samples has been used in most of the work reported here. The change in product distribution in the subsequent reaction of CH_4 and N_2O on the catalyst is shown as a function of the time of reaction in Figure 1b.

With such experimental conditions, in particular a short contact time and a high reaction temperature (843 K), the steady state is reached rapidly after 2 hours of reaction time. Several experiments done at high contact times and a

low reaction temperature (793 K) on the HPMo, HSiMo and Mo catalysts showed that the same deactivation curve shape is obtained for these catalysts with a steady state reached after 4 to 5 hours of reaction time.

After pretreatment in N_2O, O_2, H_2, CH_4 and CO, the deactivation curves of the $CH_4 + N_2O$ reaction reported in Figure 1a, c, d, e, f were obtained. However with oxygen as the pretreatment gas, the conversion of methane initially increased in contrast to the decrease observed with the other gases. It may be observed that, in general, pretreatment in an oxidizing atmosphere (N_2O, O_2) resulted in lower steady state conversions than that in reducing gases (CH_4, H_2, He, CO). This may be related to variations in stability of the heteropolyoxometalates in different atmosphere.

In general, the selectivity of the $CH_4 + N_2O$ reaction (Figure 1) toward partial oxidation products increases with the duration of reaction. In the case of the CO pretreatment (Figure 1f) the initial product distribution results, at least in part, from the oxidation of the carbonaceous species created by CO disproportionation during the pretreatment. Separate experiments have clearly shown that CO alone reacts readily on the HPMo catalyst presumably following the reaction:

$$2\ CO \rightarrow C_{ads} + CO_2$$

Consequently all the catalysts are black after a test of the $CH_4 + N_2O$ reaction. A regeneration of these used catalysts by O_2 or N_2O produced samples with color similar to the original sample in all cases. The steady state conversion in the $CH_4 + N_2O$ reaction of these regenerated catalysts is always lower than that of the original catalysts whereas the selectivity follows the same pattern with an initial selectivity similar to that of the original sample. While this decrease of conversion may be due to a thermal degradation

of the active species, since the reversibility of the selectivity indicates that the variation of this property is more likely to be due to the presence of carbonaceous species. A build up of the latter may more probably be the cause of the deactivation rather than a degradation of the supported species.

Reaction parameters. The effect of increasing the apparent contact time, W/F, where W is the mass of catalyst (gram) and F is the total flow rate ($mL.sec^{-1}$) for the $CH_4 + N_2O$ and $CH_4 + O_2$ reactions on both the HPMo and SiO_2 catalysts can be seen in Figure 2. Clearly, whatever the experimental conditions used with N_2O as an oxidant (Figure 2a and 2b) a decrease of the apparent contact time, equivalent to an increase of the total flow rate, leads to an increase of the selectivity toward partial oxidation products (here mainly formaldehyde) until a maximum is reached. A maximum is also found for the CO selectivity whereas the CO_2 selectivity has a minimum. The effect of an increase of the reaction temperature is to displace these extrema toward lower apparent contact time. This suggests that higher temperatures favor the subsequent oxidation of the partial oxidation products and CO. The CH_4 conversion increases linearly when the flow decreases until a conversion of c.a. 5% is reached.

When oxygen is used as the oxidant (Figure 2c) lower contact times favor the production of CO while a trace of formaldehyde appears. Because of the possibility of formation of this product on silica, it cannot be concluded that HPMo is the only source of the catalytic activity in producing partial oxidation products in the $CH_4 + O_2$ reaction. Again the conversion increases linearly when the apparent contact time decreases until a conversion of c.a. 5% is reached.

In order to favor the production of partial oxidation products, subsequent conversion of these products by the catalyst must be avoided. The reduction of the thickness of the catalyst bed can be employed for such purposes. As can be

seen in Figure 3, reduced catalyst mass or bed thickness does not produce the expected effect of increasing the selectivity toward the partial oxidation products when the apparent contact time is constant. The total flow rate is apparently the dominant parameter as improved partial oxidation selectivity is obtained for large catalyst mass and high total flow rate. Therefore a large mass of catalyst can be used in the production of partial oxidation products favored by high flow rates or an apparent contact time giving the maximum selectivity to formaldehyde as previously shown in Figure 2.

The effect of the reaction temperature on the selectivity of the $CH_4 + N_2O$ and $CH_4 + O_2$ reactions on the silica support and the 29.4 HPMo catalyst, has been reported in Figure 4. An Arrhenius plot of the activity versus the reciprocal of the reaction temperature gave linear relationships from which the apparent activation energies for the different suppported heteropolyoxometalates catalysts studied have been calculated. The linearity obtained with data recorded over a period of 10 hours of reaction after the steady state was reached, indicate that the catalysts were stable over that period of time in the temperature range 773-863 K.

With the HPMo catalyst, when nitrous oxide is used as an oxidant, the increase of the reaction temperature lead to an increase of the CO_2 production at the expense of the CO and formaldehyde production. This effect is however strongly attenuated when a high flow rate is used as shown in Figure 4b. On silica a similar effect of the reaction temperature can also be observed (Figure 4a).

In the reaction temperature range 773-863 K the activation energy of the reaction (from N_2 or total carbon production) is 32±2 Kcal.mol^{-1} for the supported heteropolyoxometalates except for HSiMo which give a higher value

(38±2 Kcal.mol^{-1}) closer to the Mo sample with 41±2 Kcal.mol^{-1}. A similar value has been found by Liu et al. (8) for the $CH_4 + N_2O$ reaction over a Mo/SiO_2 catalyst. For the silica support, activation energies of 11±2 and 16±2 Kcal.mol^{-1} were found in the temperature ranges 823-863 and 773-813 K, respectively. The activation energy for the CO_2 production is 35±2 Kcal.mol^{-1} for all catalysts whereas the CO activation energies vary between 29 and 47 Kcal.mol^{-1}. For the CH_2O production a low value of 22 Kcal.mol^{-1} is found. The H_2O activation energy is found to be 32±2 Kcal.mol^{-1} on Mo containing catalysts and 24±2 Kcal.mol^{-1} on W containing catalysts and the support. The quantities of CH_3OH produced were not sufficiently large to allow the measurement of activation energies.

When the reaction $CH_4 + O_2$ is performed on the support alone, the increase of the reaction temperature leads to a decrease of the CO_2 selectivity and an increase of the CO selectivity while formaldehyde selectivity remains constant until a temperature higher than 850 K is reached. On SiO_2, in the temperature range 823-863 K all products have a similar activation energy of 25±2 Kcal.mol^{-1} whereas at lower temperature (773-813 K) the activation energies for CH_2O and CO have increased to 50±2 and 126±2 Kcal.mol^{-1}, respectively.

On the HPMo catalyst the increase of temperature produces a selectivity variation similar to that observed with $CH_4 + N_2O$, but very different from that observed with the support apparently as a consequence of the strong effect of the deposited species on the reaction mechanism. Interestingly the total activation energy is 32±2 Kcal.mol^{-1} similar to the value found for the $CH_4 + N_2O$ reaction. Activation energies of 22, 58, and 33±2 Kcal.mol^{-1} were measured for CO, CO_2, and H_2O, respectively.

The variation of reactant composition has an important effect on the selec-

tivity as can be seen in Figure 5. Low values of the molar ratio N_2O/CH_4 favour the production of partial oxidation products until a maximum is reached at ca. $N_2O/CH_4 = 0.1$ for the set of experimental conditions used (Figure 5a). The CH_4 conversion increases linearly as the N_2O fraction increases from 0 to 17% whereas the CH_4 conversion decreases when the fraction of CH_4 increases (Figure 5b). These results show that the selectivity in the present system is approximately inversely related to the conversion.

From a log-log plot of the production turnover rates versus the fraction of CH_4 or N_2O in the flow, kinetic orders with respect to CH_4 and N_2O have been calculated at two reaction temperatures (793 and 843 K). No major effect of the reaction temperature on the kinetic order can be found. Therefore for the reaction temperature range 773-863 K, at atmospheric pressure and for a wide range of N_2O/CH_4 molar ratio the rate equation may be described by:

$$-\frac{d[CH_4]}{dt} = k\,[CH_4]^{\frac{1}{2}}[N_2O]^{\frac{1}{2}}$$

and the orders of the production rate of the different products of the $CH_4 \pm N_2O$ reaction have been found to be: N_2 (0.5, 0.5) CH_2O (0.5, 0.5), CO (0.70, 0.5), CO_2 (0.5, 0.30), CH_2O (0.30, 1) for CH_4 and N_2O respectively.

The effect of the presence of water has been studied in previous work on partial oxidation of methane on heterogeneous catalysts (11). In the present work the introduction of H_2O into the reactant stream induces a decrease in the conversion with the HPMo catalyst whether N_2O or O_2 is used as oxidant (Figure 6). Subsequent elimination of the water re-established the initial conversion. When N_2O is used as the oxidant the selectivity to formaldehyde appears to increase slightly for small amounts of H_2O in the flow but then decrease when the water content increases. When oxygen is the oxidant, little change in

selectivity is evident. In both cases, however, elimination of the H_2O re-establishes the original selectivity. It appears that with HPMo, water is acting as a poison rather than a promotor as has been reported for Mo/SiO_2 (8) and that no net improvement of the selectivity is induced by water at least for the set of experimental conditions used.

Reactivity of the different products. For one set of experimental conditions, the reaction of the products of the CH_4 oxidation, namely, CO, CH_2O and CH_3OH, alone in helium or in presence of N_2O or O_2 has been investigated on the silica support and the 20.0 HPMo catalyst. The results, conversion and selectivity, are summarized in Table 2.

With no oxidant added, formaldehyde and methanol in helium react readily on SiO_2, whereas the CO conversion is very small. Interestingly, methane and hydrogen are produced in small amounts from CH_2O and in large quantity from CH_3OH reacting on SiO_2. Moreover in both cases CO_2 is a minor product whereas CO is strongly favored. These results show that the support is not inert in the system studied and that both hydrogenation and oxidation processes are occurring with CH_2O and CH_3OH. These two processes are obviously detrimental to the production of partial oxidation products from the CH_4 oxidation.

The presence of HPMo on the support catalyzes the hydrogenation process, when CH_3OH and CH_2O react alone, as more CH_4 is produced than with SiO_2 as catalyst. Moreover, CO reacts on the HPMo species presumably by disproportionation, a reaction apparently catalysed by the HPMo species and possibly one of the sources of CO_2 and of the carbonaceous deposits during methane oxidation.

The main effect of the addition of N_2O to either CH_3OH and CH_2O is to increase the conversion and displace the selectivity toward more oxidised products i.e. more CO_2 and CO and less CH_4. However the hydrogenation function

is still effective as witnessed by the presence of CH_4 and a trace of H_2. Again the effect of the HPMo, relative to the SiO_2 catalyst, is to increase the conversion and at least when CH_3OH is the reactant, to increase the CH_4 produc-tion. The latter observation is consistent with earlier work from this labora-tory in which HPMo was studied in unsupported form (23,24).

When O_2 was employed as oxidant, the conversion became higher than that in the two previous cases with now a displacement of the selectivity to complete oxidation products. CH_4 production tended to disappear completely and no trace of H_2 was observed. Again the presence of the HPMo species increases the conversion of either CH_3OH and CH_2O. These results demonstrate that oxygen is a more powerful oxidant for formaldehyde and methanol than N_2O whereas the latter is more efficient in oxidising CH_4 than O_2. It is apparent that the failure to observe partial oxidation products in the $CH_4 + O_2$ reaction may be the result of their complete oxidation in subsequent steps rather than their actual absence from the initial product composition.

DISCUSSION

The results described in the present work clearly demonstrate the activity and selectivity of supported HPMo in the oxidation of methane in the presence of nitrous oxide. However, all heteropolyoxometalates with anions possessing the Keggin structure are not equally effective as catalysts in this process. For example, substitution of tungsten for molybdenum as peripheral metal element produces a reduction in both the activity and selectivity. A less severe reduction is also observed where silicon is the central atom in the anion of the heteropolyoxometalate. Such observations appear to be consistent with the results of earlier calculations from this laboratory (20,22) which showed that the strength of the bond between the peripheral metal atoms and the outer or terminal oxygen atoms of the heteropoly anion was much higher in the case of tungsten than in that of molybdenum, while the magnitude of the charge on the outer oxygen atoms in the latter case was considerably higher than that in the former, implying a reduced proton mobility when molybdenum serves as the peripheral metal element.

Although evidence presented here shows that the heteropoly compound of choice, HPMo, is participating catalytically in the oxidation process, it is evident that the SiO_2 support is playing a more active role than simply that of a high area inert solid. In particular, the support has a detrimental effect on the selectivity to partial oxidation products as carbon monoxide reacts only barely while formaldehyde and methanol are easily converted into CO and CO_2.

Pretreatment of $HPMo/SiO_2$ in a reducing atmosphere has been found to increase the activity of the catalyst but little or no influence on the selectivity is observed. Interestingly, the increase in conversion, rather than being temporary, appears to remain relatively unchanged for long periods of

time. Although the effect of pretreatment in a reducing atmosphere may speculatively be attributed to the reduction of the oxidation state of a critical element of the heteropoly anion, for example, molybdenum, it appears difficult to rationalize such a process with the duration of the effect. Previous temperature programmed desorption (TPD) studies in this laboratory (18-20) have shown that, at sufficiently high temperatures, protons contained within the unsupported heteropoly acid will extract oxygen atoms from the heteropoly anion and be desorbed as water. With HPW this process occurs at approximately 773 K while with HPMo the maximum of the corresponding desorption peak is observed at approximately 673 K. This difference was attributed to the greater lability of oxygen in HPMo as contrasted with HPW. Parenthetically it should be noted that photoacoustic FTIR studies of these two acids showed that the heteropoly anion remained intact at these temperatures in spite of the loss of up to two oxygen atoms per anion (29). Temperature programmed reduction experiments (19) with hydrogen produced peaks of similar overall shape and positions to those found in the analogous TPD experiments (18), the latter having employed helium as a carrier gas. However, whereas in the TPD experiments 1.5 water molecules per KU were desorbed with HPMo, 8.0 water molecules were measured with the high temperature TPR peak. Evidently the added hydrogen in the TPR experiments is capable of augmenting the protons in stripping oxygen atoms from the heteropoly anion. Temperature programmed exchange experiments with deuterium were also performed with the heteropoly acids (19). The temperature at which exchange began to be detected for the tungsten acids was approximately 623 K, which corresponds to the temperature at which the high temperature peak began to appear in TPR experiments. However no exchange was observed with HPMo but consumption of deuterium and reduction of the acid were observed. Thus in the

present work it appears that pretreatment in a reducing atmosphere may remove a number of terminal oxygen atoms from each heteropoly anion, thereby establishing sites for the reversible replacement and consumption of oxygen.

The oxidant in the present work appears to be of particular importance. Although oxidation occurs in the presence of oxygen, a small conversion and no partial oxidation products are observed. In contrast a mixture of methane and nitrous oxide produces formaldehyde, the amounts of which decrease with increasing temperature and with decreasing residence time. Since CH_4 and N_2O or O_2 undergo no reaction in the absence of the catalyst, the N_2O or O_2 are evidently playing the role of a source of regenerative oxygen for the catalyst. However the difference between both oxidants may be that different oxygen species or different amounts of the same active oxygen species are created by the reaction of N_2O or O_2 with the HPMo. Significantly, after pretreatment by O_2, the increase in conversion in the $CH_4 + N_2O$ reaction as shown in figure 1 may be the result of a slow replacement of the active oxygen species generated by O_2 by that generated by N_2O.

The activation energy for H_2CO formation on $HPMo/SiO_2$, 20 ± 2 kcal/mole, is similar to that observed by Somorjai et al (15) for CH_4 and N_2O on V_2O_5/SiO_2 catalyst, but considerably less than the values of 40 ± 2 and 82 ± 4 kcal/mole found with molybdena/SiO_2 catalyst at temperatures above and below 540°C, respectively (11). The kinetic orders found for H_2CO in the present work were 0.3 and 1.0, from log-log plots of N_2O and CH_4, respectively. Somorjai and co-workers obtained values of 0.2 and 0.3, respectively with the molybdena/SiO_2 catalyst and 0.33 and 0.5 for the V_2O_5/SiO_2 catalyst. Although the evidence is not conclusive nevertheless it appears that the mechanisms on the two molybdenum based catalysts may be similar. However, further work is obviously necessary to

provide information not only on the mechanism of the process on the $HPMo/SiO_2$ catalyst but also to supply information on the nature of the participation of the catalyst in the oxidation process.

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TABLE 1: Conversion and Selectivity of the supported heteropolyoxometalates and reference catalysts. Reaction Conditions: T_R= 843K, A/ W=0.35 g, F= 30 mLmin^{-1}, CH_4 (67%) N_2O (33%), B/ W= 0.35 g, F= 60 mLmin^{-1}, CH_4 (67%), O_2 (33%)

Sample	Conversion(%)			Selectivity(%)				N_2 Production Turnover Rate	
	CH_4	N_2O	O_2	CO	CO_2	CH_2O	CH_3OH	10^{-2}molec.KU^{-1} sec^{-1}	10^{-2}molec. (at metal)$^{-1}$.sec^{-1}
A/ 1.66V[a]	8.9	59.1	---	81.8	14.5	3.5	0.2	---	2.77
20.0HPMo[a]	5.1	36.4	---	65.0	22.5	12.0	0.5	6.9	0.575
20.4HPV_2Mo_{10}[a]	4.2	28.5	---	64.9	23.6	10.9	0.5	5.35	0.446
19.9HSiMo[a]	2.51	17.0	---	58.6	32.3	8.7	0.4	2.48	0.207
3 Mo	0.41	3.3	---	57.0	31.0	12.0	t	---	0.15
26.2HPW	0.40	3.2	---	56.0	44.0	t	n.d.	0.63	0.052
26.2HSiW	0.35	2.8	---	44.0	56.0	t	n.d.	0.54	0.045
SiO_2	0.12	1.1	---	32.0	68.0	n.d.	n.d.	---	---
B/HPMo[b]	0.8	---	4.5	74.0	26.0	t	n.d.		
SiO_2[b]	0.15	---	1.5	15.0	51.0	34.0	n.d.		

t: trace, n.d.: not detected
a: traces of dimethylether and H_2 were observed
b: no traces of H_2 were found.

TABLE 2: Conversion and selectivity of different reactants, CO, CH_2O, CH_3OH, involved in the partial oxidation of methane.
Reaction Conditions: T_R= 843 K, W = 0.35 g, F = 60 mLmin^{-1},
Complementary Gas: Helium

Catalyst	SiO_2 20.0 HPMo		SiO_2 20.0 HPMo		SiO_2 20.0 HPMo	
flow	CO (50%)		CO (50%) N_2O (50%)		CO(50%) O_2(50%)	
CO Conversion	0.75	8	16	16	34	34
selectivity CO_2	100	100	100	100	100	100
flow	CH_2O (10%)		CH_2O(10%) N_2O(17%)		CH_2O(10%) O_2(17%)	
CH_2O Conversion	52	87	48	68	55	83
Selectivity CO	83	51	86	82	67	18
CH_4	5	13.5	2	0.5	n.d.	n.d.
CO_2	9	34	12	16.5	33	82
CH_3OH	3	0.5	1	0.5	0.5	n.d.
H_2	lt	lt	lt	t	n.d.	n.d.
other	t	1	t	0.2	n.d.	n.d.
flow	CH_3OH (10%)		CH_3OH(10%) N_2O(28%)		CH_3OH(10%) O_2(28%)	
CH_3OH Conversion	49	94	65	80	96	100
Selectivity CO	30	22	50	47	46	61
CH_4	32	58	18	24	1.5	n.d.
CO_2	2	7	11	11	39.5	30
CH_2O	16	7	16	17	9	9.3
H_2	lt	lt	lt	t	n.d.	n.d.
other	t	6	5	1	n.d.	n.d.

t: trace, lt: large trace, n.d.: not detected.

a: C deposits are not accounted for in the selectivity

b: C_2, C_3, C_4 hydrocarbons and dimethylether.

FIGURE CAPTIONS

Figure 1: Conversion and selectivity of the $CH_4 + N_2O$ reaction over the 29.4 $HPMo/SiO_2$ catalyst vs the time of reaction after different pretreatment.

Reaction Conditions: T_R = 843 K, W = 0.35 g, F = 30 $mLmin^{-1}$ CH_4 (67%) N_2O (33%). Pretreatment for 1 hour at 843 K in (a) N_2O, (b) Helium, (c) O_2, (d) H_2, (e) CH_4, (f) CO.

Symbols: (△) CO, (0) CO_2, (□) CH_2O, (●) CH_4 conversion

Figure 2: Effect of the contact time on the conversion and selectivity of the 29.4 $HPMo/SiO_2$ catalyst for the $CH_4 + N_2O$ and $CH_4 + O_2$ reactions.

Reaction Conditions: A/ T_R= 793 K, W=1.0 g, CH_4(67%) N_2O(33%)

B/ T_R=843 K, open symbols W=1.0 g, black symbols W=0.17 g, CH_4(67%) N_2O(33%), C/ T_R=843 K, W=1.0 g, CH_4(67%) O_2(33%)

Symbols: (△) CO, (0) CO_2, (□) CH_2O, (x) CH_4 conversion.

Figure 3: Conversion and selectivity of the $CH_4 + N_2O$ reaction vs the mass of 29.4 $HPMo/SiO_2$ catalyst (or bed thickness) at constant apparent contact time.

Reaction Conditions: T_R=843K, CH_4(67%) N_2O(33%)

W/F=0.67 $g.mL^{-1}.sec.$

Symbols: (△) CO, (0) CO_2, (□) CH_2O, (x) CH_4 Conversion

Figure 4: Effect of the reaction temperature on the selectivity of the $CH_4 + N_2O$ or $CH_4 + O_2$ reactions on the 29.4 $HPMo/SiO_2$ and the SiO_2 support.

Reaction conditions: A/ SiO_2, F=15$mLmin^{-1}$, W=2.0 g, open symbols: CH_4(67%) N_2O(33%), black symbols: CH_4(67%) O_2(33%)

B/ HPMo, open symbols: F=7.5 $mLmin^{-1}$, black symbols: F=90$mLmin^{-1}$,

W=1.0 g, CH_4(67%) N_2O(33%), C/ HPMo, F=15mLmin^{-1}, W=1.0 g, CH_4(67%) O_2(33%)

Symbols: (△) CO, (○) CO_2, (□) CH_2O.

Figure 5: Effect of the CH_4 or N_2O concentration in flow on conversion and selectivity of the sample 29.4 HPMo/SiO_2.

Reaction conditions: F=60mLmin^{-1}, W=1.0 g, T_R=843 K, A/ CH_4(50%) He (5-N_2O%) B/ N_2O(25%) He(75-CH_4%)

Symbols: (△) CO, (0)CO_2, (□) CH_2O, (●) CH_4 conversion

Figure 6: Effect of the amount of water in flow on the conversion and selectivity of the A/ CH_4 + N_2O and B/ CH_4 + O_2 reactions on the 29.4 HPMo/SiO_2 catalyst.

Reaction conditions: T_R=843 K, W=1.0 g and A/ F=30mlmin^{-1}, CH_4 (40%) O_2 (21%) Me (40-H_2O%) B/ F=60 mLmin^{-1}, CH_4(51%) N_2O(26%) Me(23-H_2O%)

Symbols: (△) CO, (0) CO_2, (□) CH_2O, (●) CH_4 conversion.

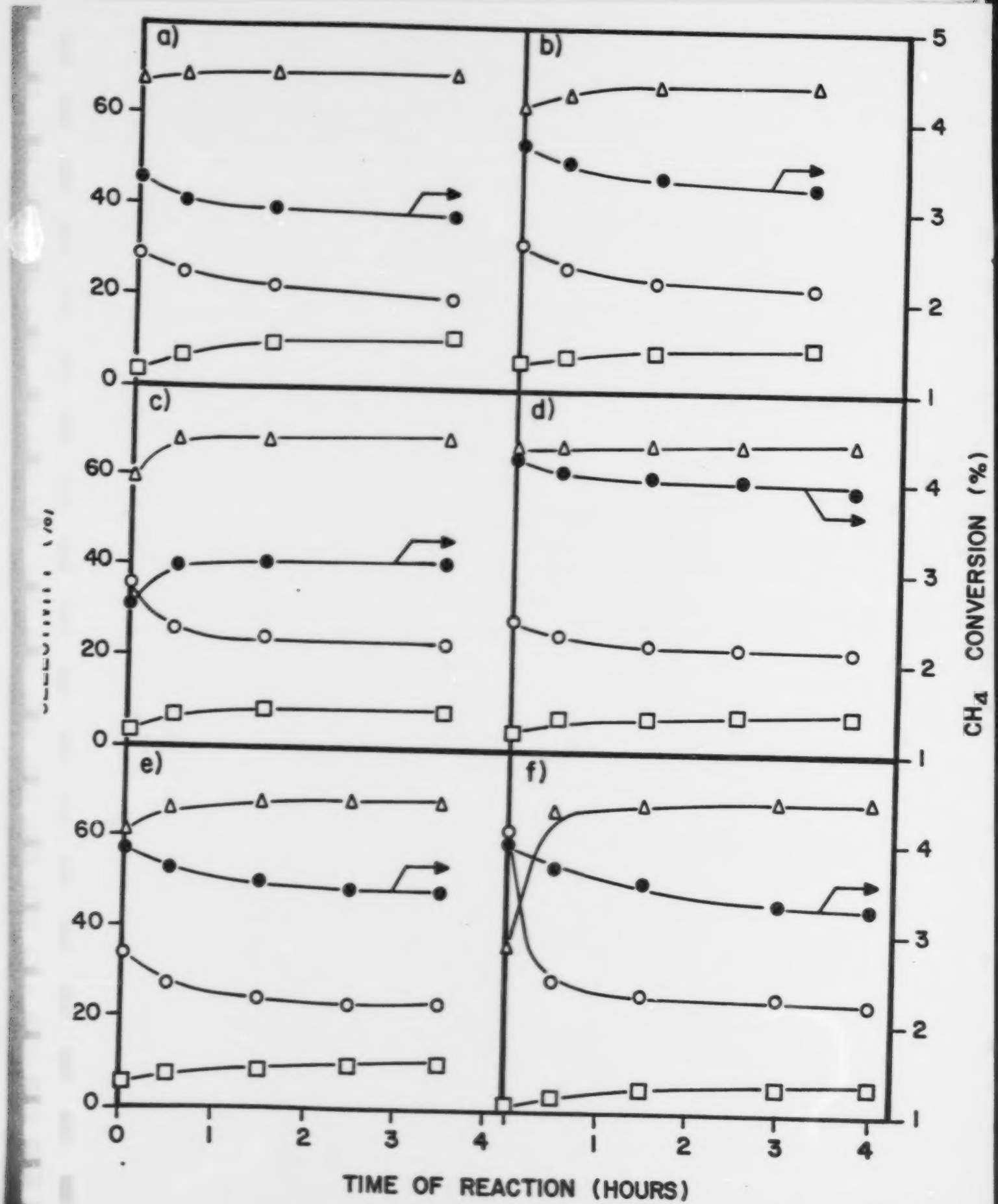
a)
b)
c)
d)
e)
f)
60
40
20
0
5
4
3
2
1
0
1
2
3
4
TIME OF REACTION (HOURS)
CH4 CONVERSION (%)

FIG. 1

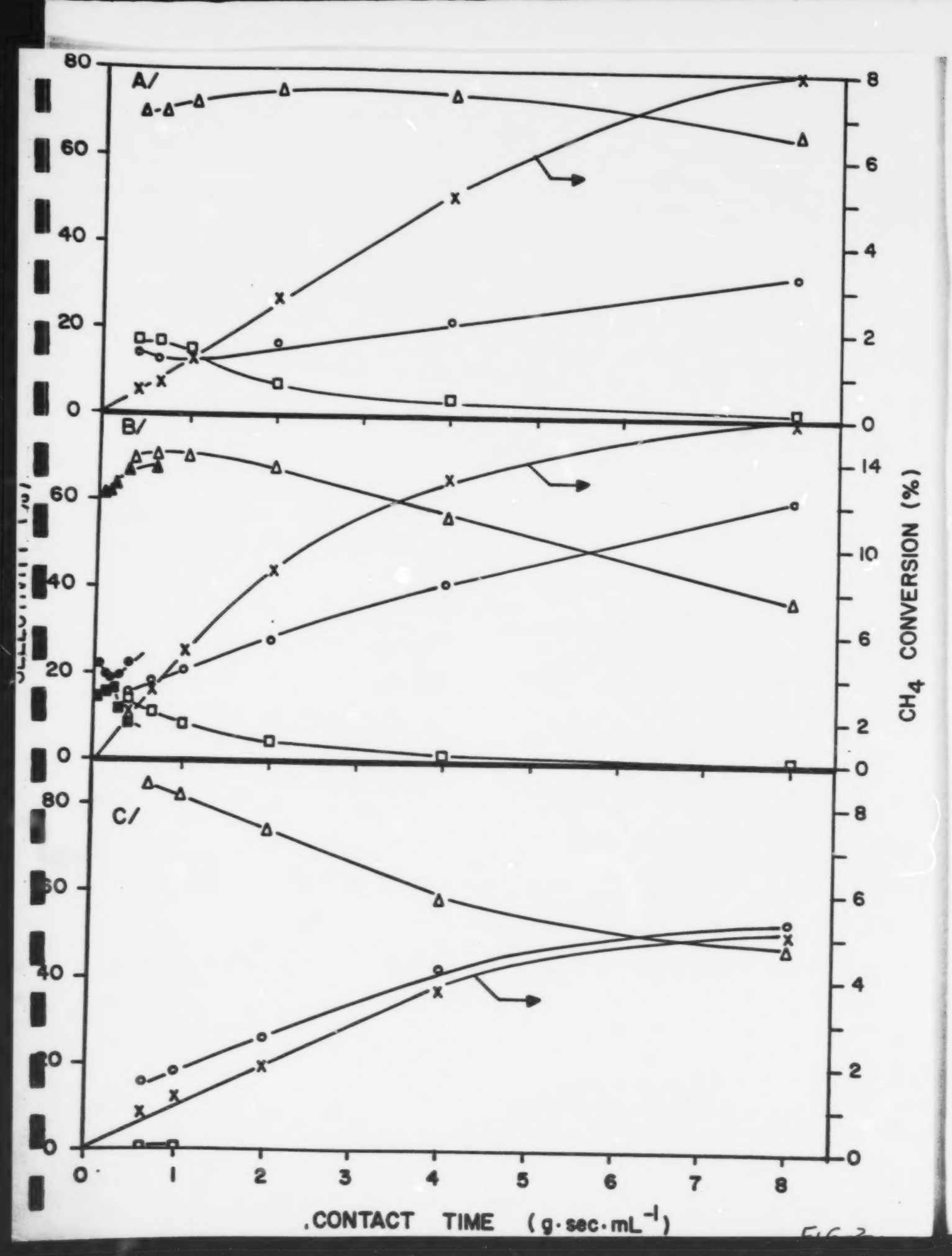
A/
B/
C/
80
60
40
20
0
8
6
4
2
0
14
10
6
2
0
1
2
3
4
5
6
7
8
CH4 CONVERSION (%)
.CONTACT TIME (g·sec·mL⁻¹)

FIG 3

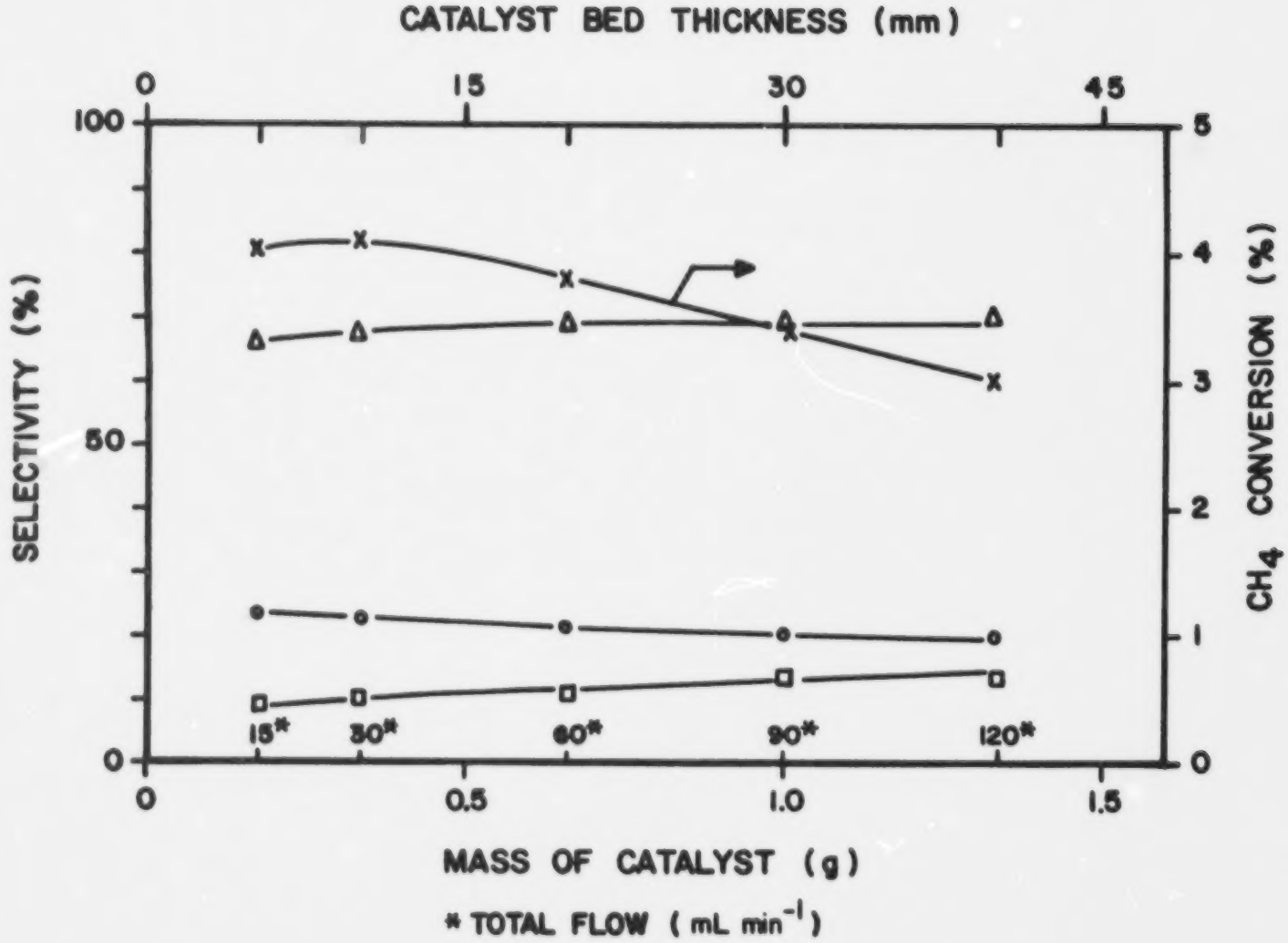
CATALYST BED THICKNESS (mm)
0
15
30
45
100
50
0
SELECTIVITY (%)
5
4
3
2
1
0
CH4 CONVERSION (%)
0
0.5
1.0
1.5
MASS OF CATALYST (g)
15*
30*
60*
90*
120*
* TOTAL FLOW (mL min-1)

FIG. 3

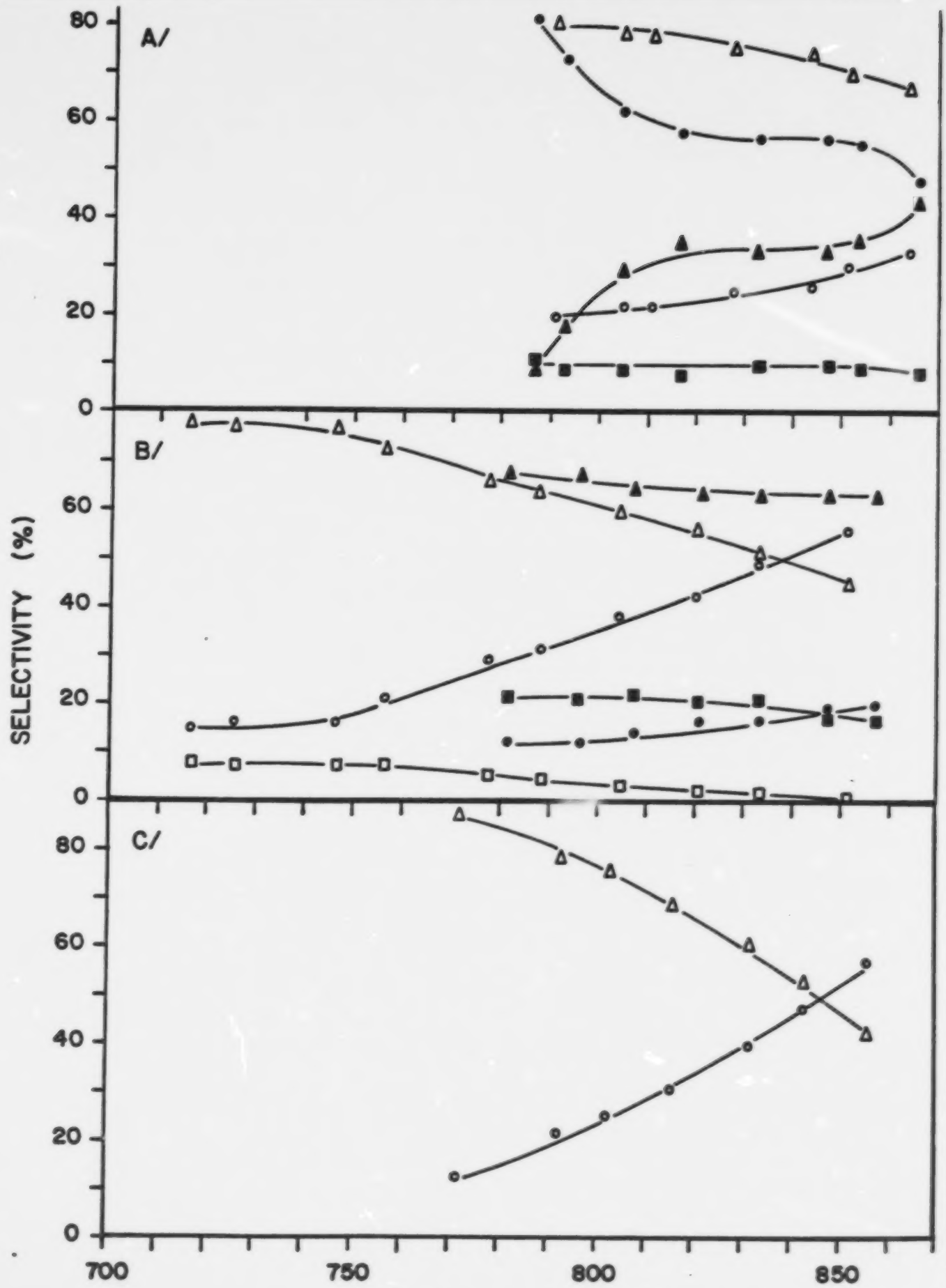
A/
B/
C/
SELECTIVITY (%)
0
20
40
60
80
700
750
800
850
REACTION TEMPERATURE (K)

FIG 4

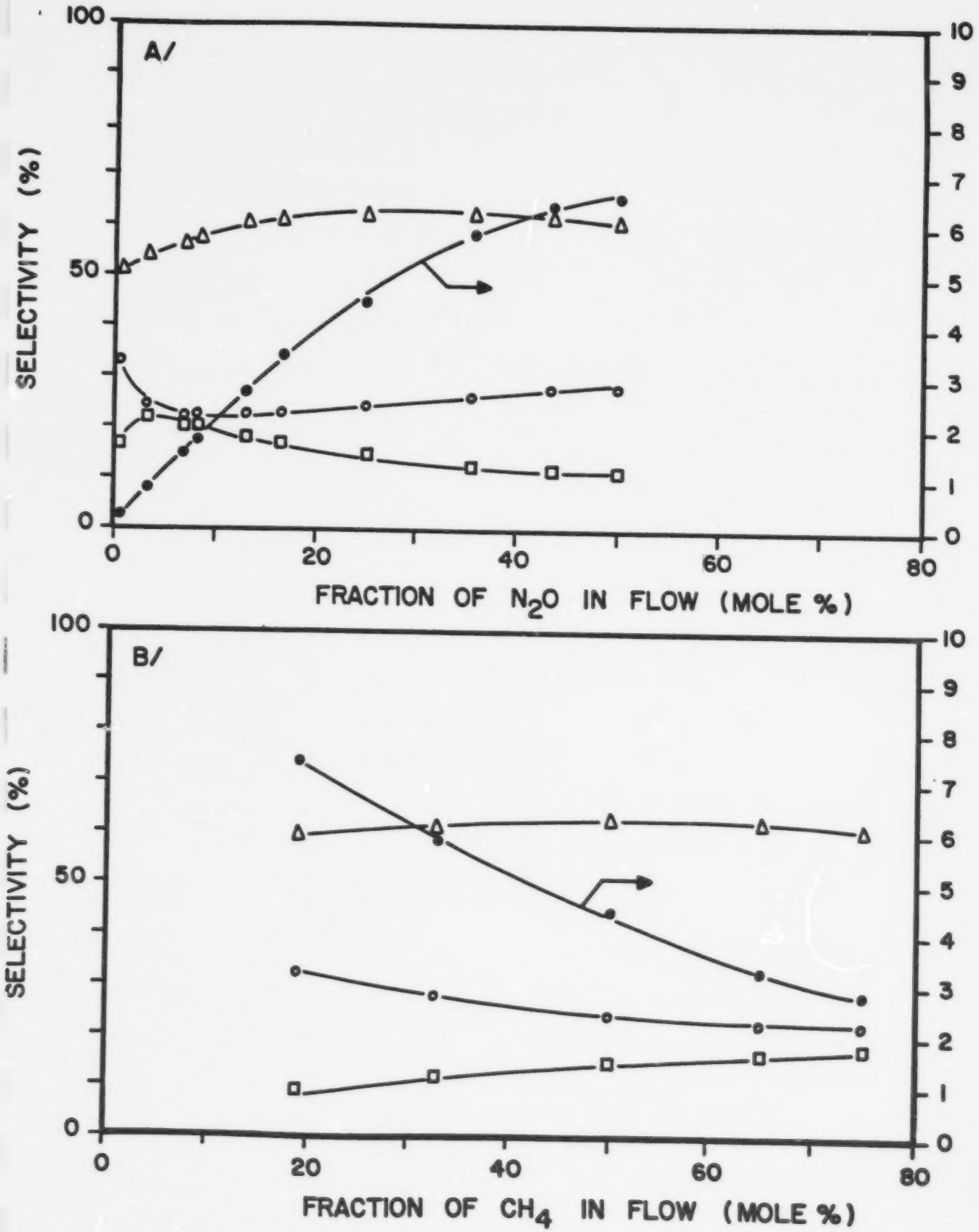
A/
SELECTIVITY (%)
CH4 CONVERSION (%)
FRACTION OF N2O IN FLOW (MOLE %)
B/
SELECTIVITY (%)
CH4 CONVERSION (%)
FRACTION OF CH4 IN FLOW (MOLE %)

FIG. 5

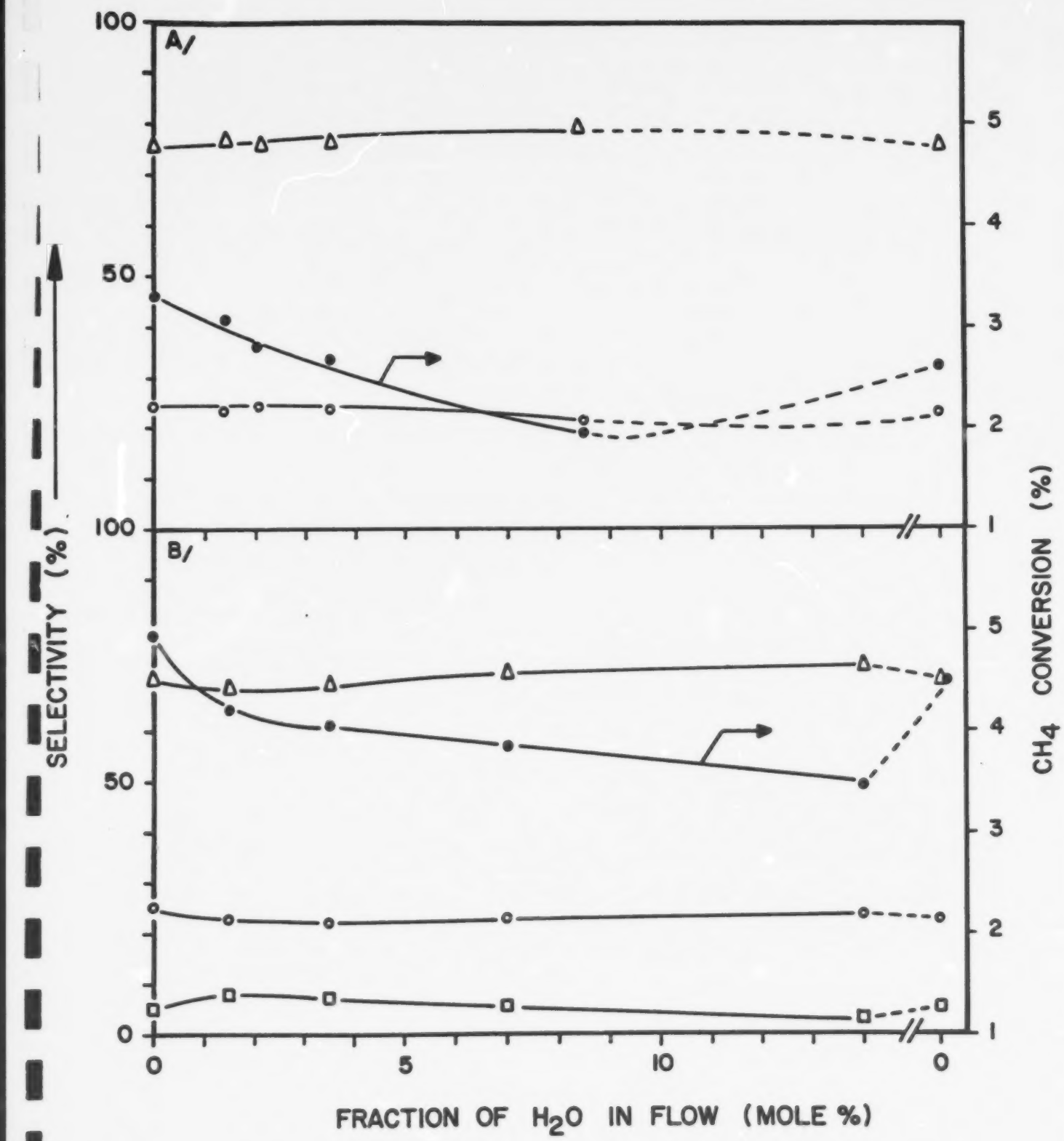
100
A/
50
100
B/
50
0
0
5
10
0
SELECTIVITY (%)
5
4
3
2
1
5
4
3
2
1
CH4 CONVERSION (%)
FRACTION OF H2O IN FLOW (MOLE %)

FIG. 6

THE OXIDATION OF METHANE ON HETEROPOLYOXOMETALATES

II. NATURE AND STABILITY OF THE SUPPORTED SPECIES

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ABSTRACT

The heteropolyoxometalate, 12-molybdophosphoric acid, supported on silica, has been shown to be an effective catalyst in the oxidation of methane. It is demonstrated, from studies of the effects of loading and calcination, that the heteropoly anions (Keggin Units) are the species primarily responsible for the catalytic activity. It is also shown that the supported heteropoly anions possess an enhanced thermal stability. An optimum loading is observed, at which approximately ten percent of the available support area is occupied.

INTRODUCTION

The activation of the C-H bond and the partial oxidation of methane are problems of considerable current interest (1,2). While much of the work on C-H bond activation has been related to homogeneous metal complexes (3), Lunsford and co-workers (4) and Somorjai et al (5, 6) have recently generated considerable interest in the possibility of activation of the C-H bond through the use of the heterogeneous catalysts, molybdena/silica, and vanadium pentoxide/silica. Earlier work from this laboratory on heteropolyoxometalates (7) has provided the incentive for the study of these compounds as possible heterogeneous catalysts for the partial oxidation of methane.

In the first part of this work (8), the results of studies of the partial oxidation of methane with a number of heteropolyoxometalates, supported on silica, have been reported. These heteropoly compounds include 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiMo), 12-tungstophosphoric (HPW), 12-tungstosilicic (HSiW), and 10-molybdo-2-vanadophosphoric acid ($HPMo_{10}V_2$). Within the range of experimental conditions used, it has been found that molybdenum containing heteropoly acids are active and selective catalysts for the partial oxidation of methane, with activities greater than the molybdena/silica catalysts but less than those of vanadium pentoxide/silica and selectivities rather similar in all cases. In contrast, tungsten based heteropoly acids showed little or no activity in the partial oxidation of methane.

In work from this laboratory (8) the supported HPMo catalyst was found to be the most active of the molybdenum based heteropoly acids. Relatively little work on either the application or characterization of supported heteropoly compounds has been reported in the literature. Izumi and Urabe (9) reported that certain heteropoly acids could be entrapped in active carbon and a subsequent publication (10) from the same laboratory was concerned with several reactions catalyzed by various heteropoly acids supported on silica gel, activated carbon, alumina, and titania. More recently, the isomerization of alkanes has been studied with a palladium salt of a heteropoly acid supported on silica (11).

As a consequence of the importance in the partial oxidation of methane, of supporting of HPMo, as noted in the previous report from this laboratory, the earlier work has been extended to examine various aspects of these supported catalysts, but particularly the nature and stability of the supported species.

EXPERIMENTAL

Catalysts

The supported catalysts were prepared by impregnation of a silica gel (Grace Davison grade 400, 740 $\pm$ 20 m^2g^{-1}) with an excess of solution of recrystallized HPMo (BDH Analar grade). The slurry was then evaporated to dryness at 80°C overnight and calcined in air at 350°C for 1 hour. In the present work catalysts with loadings up to approximately 50 wt% have been prepared. For convenience these SiO_2 supported catalysts will be symbolized by their wt% of acid followed by HPMo. In all cases aliquots employed in both the analyses and reaction experiments were those in the 8-15 mesh size after sieving.

With the 23 wt% HPMo catalyst, small samples, in addition to those referred to above, were calcined in air for 16 hours at temperatures from 623 to 1003 K. At a calcination temperature of 823 K, samples were taken after 3, 16, 43 and 90 hours of calcination.

A sample of the support, to be used as the support standard, was impregnated with an acidic solution (HNO_3, 1M, pH=2) and calcined at 350°C for 1 hour.

Quantitative Analysis

Molybdenum was extracted from the supported catalysts by elution with concentrated ammonium hydroxide solution. After evaporation and addition of aqueous nitric acid solution to achieve a standard volume, the samples were analyzed for molybdenum with an appropriately calibrated Direct Coupled Plasma Spectroscan (Beckman Model 5). The calculated loadings and the loadings measured before and after use are reported in Table 1.

Catalytic Experiments

Details of the reactor, ancillary equipment and procedures have previously been described (8). In brief, the catalytic reactions have been performed in a continuous flow system fitted with a quartz reactor (9 mm OD). The gases required, He (99.9%), CH_4 (90.0%), N_2O (99.0%), O_2 (99.0%) were obtained from Matheson and used as received. The catalysts were pretreated in a flow of helium for one hour at the reaction temperature. All products and remaining reactants were analyzed by an on-line gas chromatograph (Hewlett Packard 5890) equipped with a thermal conductivity detector. The conversions and selectivities were determined under steady state conditions, generally attained after three hours under the experimental conditions previously described (8). The selectivities are reported as mole percent of each of the major products, CO, CO_2, H_2CO, and CH_3OH, formed. Traces of C_2H_6, C_2H_4 and other hydrocarbons, which are mainly impurities contained in CH_4, as well as traces of dimethyl ether, are omitted. Production rates are reported, for convenience, per gram of support while the loadings of HPMo on the silica are expressed as moles of Keggin Unit (KU) per gram of support. Homogeneous reactions have been shown to generate negligible quantities of products (8).

Infrared Analysis

Approximately 0.3 g of the supported catalyst was washed with 10 ml of acetonitrile (Baker Analyzed) to remove the soluble HPMo from the support. After filtration, the IR spectra (Perkin-Elmer Model 983) of the solution were recorded. No evidence of significant decomposition of the heteropoly acids nor of generation of these compounds from molybdate and phosphate was found in acetonitrile solutions after 24 hours.

FTIR Photoacoustic Analysis

Photoacoustic Fourier Transformed Infrared Spectra of the bulk HPMo have been recorded in order to determine the stability of this compound in different media and at various temperatures. The samples were pretreated under vacuum or in a CH_4 + N_2O atmosphere at a number of temperatures. After cooling, the samples were outgassed prior to transfer to the photoacoustic cell in a dry box filled with argon. PAS-FTIR spectra (Bomem DA3.02) from 4000 to 550 cm^{-1} were obtained by methods previously described (7).

RESULTS

The effects of the temperature and duration of calcination on the activity, selectivity, and loading of the 23 HPMo catalyst in the CH_4-N_2O reaction are shown in Figure 1. The conversion and selectivity in the oxidation of methane with nitrous oxide on silica-supported HPMo remains relatively constant for calcination temperatures up to 700 K (Fig. 1a, b). For higher temperatures the conversion decreased sharply while the production of CO and CO_2 remains constant up to approximately 900 K. Above 900 K the production of H_2CO and CO decreases, while that of CO_2 increases, all three apparently approaching that found with the support alone. Above 700 K there is a concomitant small, but significant, decrease in the amount of supported molybdenum, whereas the conversion becomes negligibly small.

At a calcination temperature of 823 K, [at which temperature thermal degradation is evidently occurring (Fig. 1a, b)], the conversion of methane decreases relatively slowly with the duration of calcination while a small loss of HPMo can be observed (Fig. 1d). Concurrently, the production of CO increases

slightly while that of CO_2 and of H_2CO decreases slowly. Evidently the activity of the HPMo catalysts can be attributed to a thermally sensitive species whose degradation products have a considerably reduced activity in the oxidation of methane.

The rates of formation of the various products from the reaction of CH_4 and N_2O at 843 K are shown for various loadings of HPMo on silica (Fig. 2a). With the exception of that of methanol, these rates increase approximately linearly with the amount of HPMo contained on the supported and at low loading values, extrapolate to those results found for the support itself. The rates of formation for the various products reach maxima at a loading of approximately 120 micromoles of KU per gram of support. The position of the maximum for methanol and formaldehyde are less clearly defined, but will be taken as that given above. With further increase in the loading the rates of formation decrease markedly to approximately constant values at loadings as high as 200 micromoles KU per gram of support. It is of particular interest to note that while the rate of production of formaldehyde has become negligible at such relatively high loadings, the rate of formation of CO_2 has decreased relatively little as compared with that of CO, for example.

Similar features have been observed for a reaction performed at 793 K (reaction parameters: W = 0.5 g, F = 15 ml min^{-1}, CH_4 67%, N_2O 33%) with, however, a maximum for formaldehyde occurring at a lower loading of approximately 50 micromoles KU per gram of support, whereas all other products displayed a maximum at a loading of 120 micromoles KU per gram of support, similar to that observed at the higher temperature. The slopes of the linear graphs in Figure 2 may be employed to calculate turnover numbers, that is rates of formation based on the number of anions or Keggin Units held on the support. These are summarized in Table 2 together with the results obtained at 793 K.

When oxygen is employed as an oxidant, the rates of formation of the various products are much lower than with N_2O, as previously reported (8) (Figure 3). The rates again increase approximately linearly up to 140-160 micromoles KU and apparently remain constant with further increases in loading. However, extrapolation of the linear plots to zero loading now produces intercepts considerably higher than the values for the support itself. It is of interest to note that the ratio of the rates of formation for CO/CO_2 is approximately one where oxygen is employed as the oxidant but increases to two with nitrous oxide. Little or no formaldehyde and methanol are formed with oxygen. Similar features have been observed for a reaction temperature of 793 K.

It is instructive to examine the product distributions obtained with the two oxidants for various loadings on the silica support (Figs. 4a, b). At 843 K, for example, the % CO in the product from the $N_2O + CH_4$ reaction increases sharply with the loading and reaches a constant value at relatively small loadings of HPMo. In contrast the CO_2 contained in the product decreases, passes through a minimum and attains a constant level for loadings of approximately 200 micromoles KU per gram of support. The quantity of formaldehyde appears to be reciprocally related to that of CO_2 in their dependences on the amount of supported HPMo, with the quantity of formaldehyde increasing to a maximum at a loading of 20 micromoles KU per gram of support and with further increase in loading decreasing to a negligible level at that quantity of HPMo at which CO_2 achieves a constant value.

With oxygen at 843 K, however, the concentration of CO decreases monotonically with loading of HPMo, while that of CO_2 increases, and a small amount of formaldehyde is observed whose maximum appears at a loading similar to that with

N_2O. However it is possible that this small amount of formaldehyde is generated by the support rather than the supported HPMo. Similar features have been observed at 793 K with both O_2 and N_2O.

At least for one set of conditions it is evident that the loading of the support has large effect both on the activity and selectivity. However while under the present conditons the maximum in activity occurs for a relatively large loading of 120 micromoles KU per gram of support, that for the selectivity to partial oxidation product is reached at a much lower loading of 20 micromoles KU per gram of support. It is anticipated that reaction temperature and residence time will not alter the position of the maximum for activity but will undoubtedly effect that for selectivity. As has been shown earlier (9), better selectivity to partial oxidation products can be expected at higher total flow rates and lower reaction temperatures.

Infrared spectra of acetonitrile solutions obtained by washing the silica-supported HPMo confirm the existence of $PMo_{12}O_{40}^{3-}$ anions with the Keggin structure on a variety of samples (Fig. 5). IR spectra of the 12-molybdophosphoric acid in acetonitrile shows the bands at 1080 and the doublet at 969-960 cm^{-1} characteristic of the Keggin structure and attributed to the triply degenerate asymmetric stretch of the central PO_4 tetrahedron and that of the outer Mo-O band (7). Spectra of samples covering a wide range of loadings reported in Fig. 5, show these characteristic bands. With the sample of smallest loading, 1.16 HPMo/SiO_2, the spectra obtained from the extraction of this catalyst show relatively weak but nevertheless characteristic Keggin structure IR bands. With those samples more heavily loaded (11.1 HPMo) the characteristic bands are considerably more intense, even after heating of the

sample to 350°C for 2 hours. With a 20.1 HPMo sample heated for 16 hours under air some diminution of the intensities occurs as temperatures up to 650°C are reached, but there can be no doubt as to the existence of the Keggin structure even at such a high temperature treatment. After use of the 20.1 HPMo catalyst in an oxidation experiment at 570°C, the Keggin structure is still clearly evident, and even after heating the sample to 730°C, some vestiges of the presence of Keggin structure still exist.

For comparison purposes photoacoustic FTIR spectra of bulk HPMo after heating at various temperatures are shown in Fig. 6. Characteristic spectra similar to those found with untreated HPMo are observed for bulk samples heated to 350°C under vacuum. However, after heating to 450°C the intensities of the characteristic bands have been considerably reduced, and after heating at 550°C in N_2O and CH_4 or in vacuum, no evidence of Keggin structures may be seen.

DISCUSSION

The beneficial effects of the participation of the heteropolyoxometalate $H_3PMo_{12}O_{40}$ in the oxidation of methane can be clearly seen from the results presented in this work. The infrared spectra provide evidence that the deposited species at various loadings of the support are the 12-molybdophosphate anions with Keggin structure. Furthermore these results clearly demonstrate that portions of the original amounts of these species still exist after vigorous treatment such as calcination at 640°C for 16 hours or exposure to methane and nitrous oxide under oxidation conditions.

That the Keggin Unit is primarily responsible for the catalytic activity in the partial oxidation of methane is evident from the studies of the effects of loading, calcination temperature and duration. The linear increase in the rate of formation of various products with increase in loading clearly indicates that the active species are associated directly with the supported materials. Since, at temperatures of approximately 650°C, the selectivities of the supported catalyst abruptly change to those expected from the support itself, while from the infrared spectral data it is evident that the Keggin Units are diminishing in number, it is apparent that the active species are those anions possessing the Keggin structure. The production rate increases linearly to a maximum at 120 micromole KU per gram of support. This optimum loading of HPMo on SiO_2 corresponds to a coverage of approximately 1000 A^2/KU, a substantially larger area than the 100 A^2 estimated for the cross-sectional area of a Keggin Unit. Therefore each KU is likely to be isolated on the support surface. Although such an optimum loading may be referred to as a monolayer coverage, it may be advantageous, as will become more evident later, to view such a loading in terms of the saturation of a number of fixation centers as has been proposed elsewhere

for unrelated supported catalysts (12). This number is characteristic of the support, the species adsorbed, the pretreatment and the conditions of preparation of the supported system. For the silica support used in the present work, the maximum number of fixation sites of the KU is therefore the saturation limit, that is 120 micromole site g^{-1} or approximately 0.098 sites nm^{-2}. In comparison, 0.3 sites nm^{-2} have been estimated for Al_2O_3 (13). While emphasis here has been placed on the quantity of heteropoly species contained on the support surface, it should be noted that the method of preparation of the supported samples is not unimportant. For example, it may be observed (Fig. 2) that one particular sample, near the optimum value, produced results considerably lower than expected. It appears that the method of preparation may occasionally lead to poorly dispersed samples. However the linear dependence of production rate appears to confirm that the optimum dispersion has been, in general, achieved at least for loadings less than 120 micromole KU per gram of support.

For loadings greater than 200 micromoles KU per gram of support (600 A^2/KU), the production rates of N_2, total carbon, H_2O, CO, and CO_2 have decreased to apparently constant values considerably less than those found at the individual maxima, but greater than those for the support itself. At this same loading, the rate of production of formaldehyde has decreased to a negligible level, as was found after calcination at 900 K (Fig. 1). Evidently this corresponds to the attainment of a stationary surface concentration which is apparently less than optimum for the oxidation process.

The observations of the effect of calcination temperature clearly demonstrate that the elemental composition possessed by the heteropoly compound is not sufficient to guarantee catalytic selectivity in the oxidation of methane, as well as showing that the stabilized Keggin structure is sufficient, but not

necessarily uniquely so, for this purpose. However it is not clear at this time whether the disadvantage of heavier loadings of HPMo on SiO_2 is a consequence of the inability of the support to stabilize quantities of the heteropoly compound greater than that at saturation, or is due to the effect of the formation of particles of HPMo which may exert a blocking effect on those in direct contact with the support. It is important to note here that while polar molecules can readily penetrate into the bulk structure of heteropoly compounds (7), nonpolar species such as alkanes are unable to do so. Consequently the formation of particles of HPMo on the surface of the support will render any KU contained within the bulk of the particle inaccessible to methane and hence inactive in the oxidation of methane. However, the observed charges in selectivity at high loading may, at least in part, arise from secondary processes resulting from the penetration and reaction of polar products, H_2CO and CH_3OH, within the bulk of HPMo particles to produce CO and/or CO_2.

As has been noted, the infrared spectra provide evidence that the supported species retain the Keggin structure. Clearly the supported species not only have this structure but retain it even after heating to temperatures as high as 700°C and after reactions at 570°C. In contrast, bulk HPMo has apparently lost much of its Keggin structure by 450°C. The SiO_2 support is clearly acting, notonly as a means of increasing the available surface area of the heteropoly compound, but also as a stabilizer for the Keggin structure of the anion. It is, of course, not possible at this time to comment definitively on the nature and source of such stabilization. However, two broad categories of such binding may be recognized, namely an electrostatic effect between surface charges and those on the anion and/or the formation of a bond between the silica surface and

the anions. In view of the fact that the supported species may readily be stripped from the surface of the support by the polar acetonitrile, the former effect appears to be more plausible than the latter.

The relevance of the structural results and conclusions presented herein to other supported catalytic systems such as molybdenum-, tungsten-, and vanadium-based catalysts supported on SiO_2 or Al_2O_3 is worthy of comment. The nature of the supported species in these systems continues to be in dispute after many years of research effort. Recently, it has been proposed that isopolyanions existing in solution during the preparation of the MoO_3/Al_2O_3 catalysts are the predominant species existing after calcination at temperatures as high as 500°C (14-16). Since it has been widely believed that the isopolyanion structure, known to be thermally fragile, would decompose at such temperatures, many authors have concluded that the supported species are decomposition products. The remarkable stability of the Keggin structure of 12-molybdophosphoric acid when supported on silica provides additional support to the hypothesis that many supported catalysts after calcination may have a substantial portion of their metal content contained within iso- or heteroanionic structure. Such classes of catalysts could be referred to as supported polyoxometalates (14).

The present work has demonstrated that the heteropoly anions of Keggin structure are the species primarily responsible for the catalytic activity. While these species enjoy an enhanced stability on the silica support their surface concentration must be relatively small in order to achieve optimum activity and selectivity.

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TABLE 1 : Loading of the different samples before and after catalytic test.

Prepared Sample wt% HPMo	Loading Found wt% HPMo	10^{-6}mol KU g^{-1}_{s}	KU nm^{-2}	After test at 843K[d] wt% HPMo
1.45	1.16	5.16	0.0042	1.22
2.85	1.72	7.74	0.0063	1.51
4.22	3.08	14.0	0.0115	2.52
5.54	2.94	13.4	0.011	2.89
8.09	6.49	30.7	0.025	4.44
9.89	8.32	40.2	0.033	---
12.8	11.10	55.3	0.045	9.92
16.2	9.80	48.1	0.039	9.06
18.2	17.21	92.1	0.075	14.4
20.0	16.0	84.3	0.068	---
22.7	21.2	119	0.097	15.2
26.1	25.3	150	0.122	18.6
29.4[a]	20.1	111	0.090	15.9
29.4[b]	21.7	123	0.100	---
29.4[c]	23.0	132	0.108	---
37.1	30.9	198	0.161	25.3
46.4	39.0	283	0.130	---

a,b,c different preparation

d same experimental conditions as figure 2

TABLE 2 : Turnover rate of production of the different products of the $CH_4 + N_2O$ reaction at two different reaction temperatures.

Products	Turnover rate 10^{-2} mol. KU^{-1}. sec^{-1} 793 K[a]	843 K[b]
N^2	7.85	42.0
H_2O	5.10	26.4
CO	1.64	7.7
CO_2	0.60	3.5
CH_2O	0.42	1.1
CH_3OH	--	0.24

reaction conditions: [a] CH_4 (67%) N_2O (33%), W = 2.0 g, F = 15 $mLmin^{-1}$
[b] CH_4 (67%) N_2O (33%), W = 0.5 g, F = 30 $mLmin^{-1}$

FIGURE CAPTIONS

Figure 1: Effect of the temperature of calcination during 16 hours (left) and of the time of calcination at 823 K under air (right) on the CH_4 conversion, selectivity and Mo loading of the 23 HPMo Catalyst. Reaction Conditions: CH_4 (67%) N_2O (33%) T_R= 843K, W = 0.5g, F = 30 $mLmin^{-1}$

Symbols: (Δ) CO, (0) CO_2, (□) CH_2O, (x) CH_4 conversion (●) Mo loading.

Figure 2: Effect of the HPMo loading of the support on the production rate of the different products of the CH_4 + N_2O reaction at 843 K
Reaction conditions: CH_4 (67%) N_2O (33%), W = 0.5 g, F = 30 $mLmin^{-1}$.

Symbols: (x) N2, (+) total carbon detected, (●) H_2O, (▽) CH_3OH, (Δ) CO, (0) CO_2, (□) CH_2O.

Figure 3: Effect of the HPMo loading of the support on the production rate of the different products of the CH_4 + O_2 reaction at 843 K
Reaction conditions: CH_4 (67%), O_2 (33%), W = 0.5 g, F = 15 $mLmin^{-1}$

Symbols: (●) H_2O, (+) total C detected, (Δ) CO, (0) CO_2, (□) CH_2O

Figure 4: Effect of the HPMo loading of the support on the selectivity of the A/CH_4 + N_2O and B/CH_4 + O_2 reaction at 843 K. Same experimental conditions as figure II and III respectively.

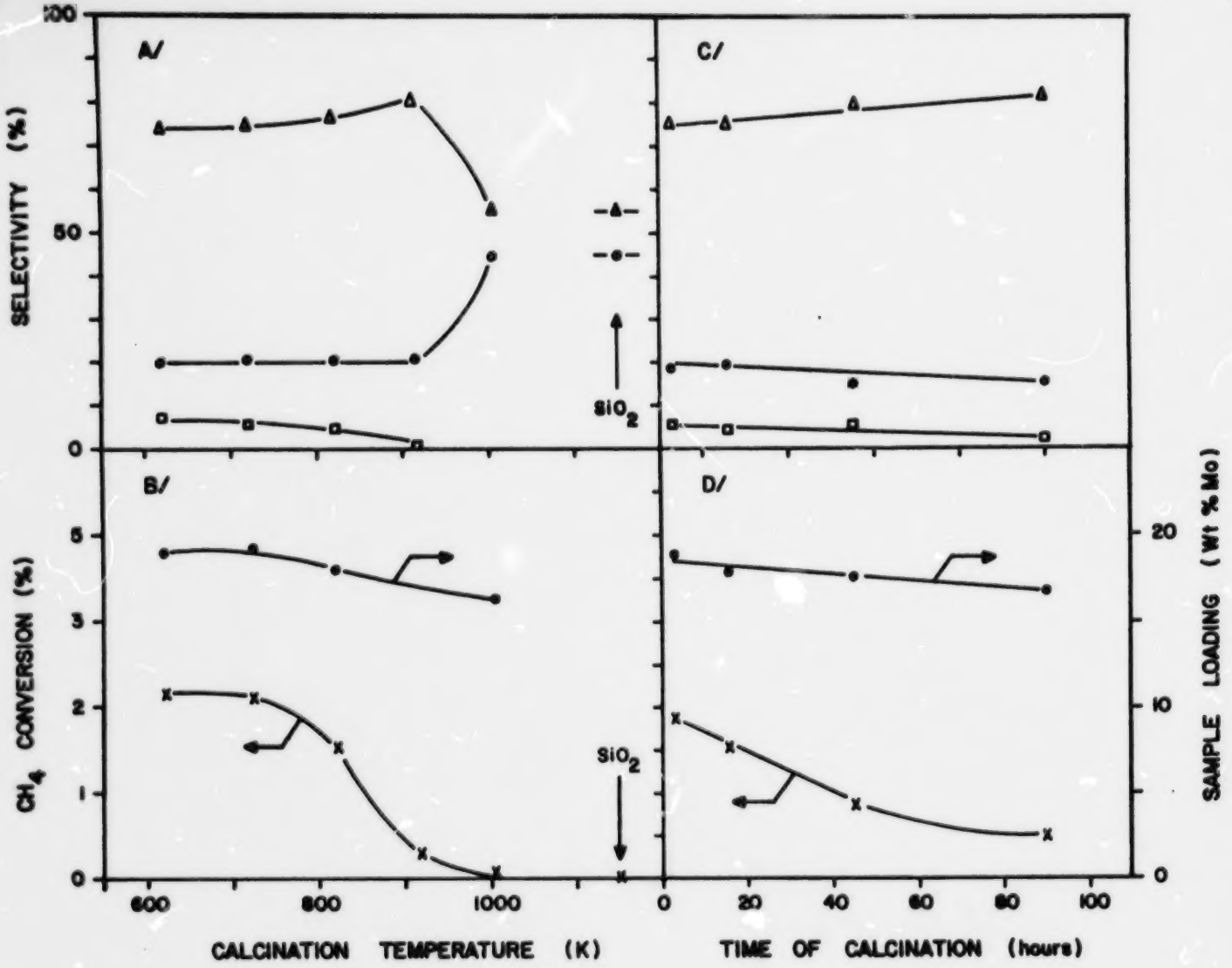
Symbols: (Δ) CO, (0) CO_2, (□) CH_2O, (▽) CH_3OH

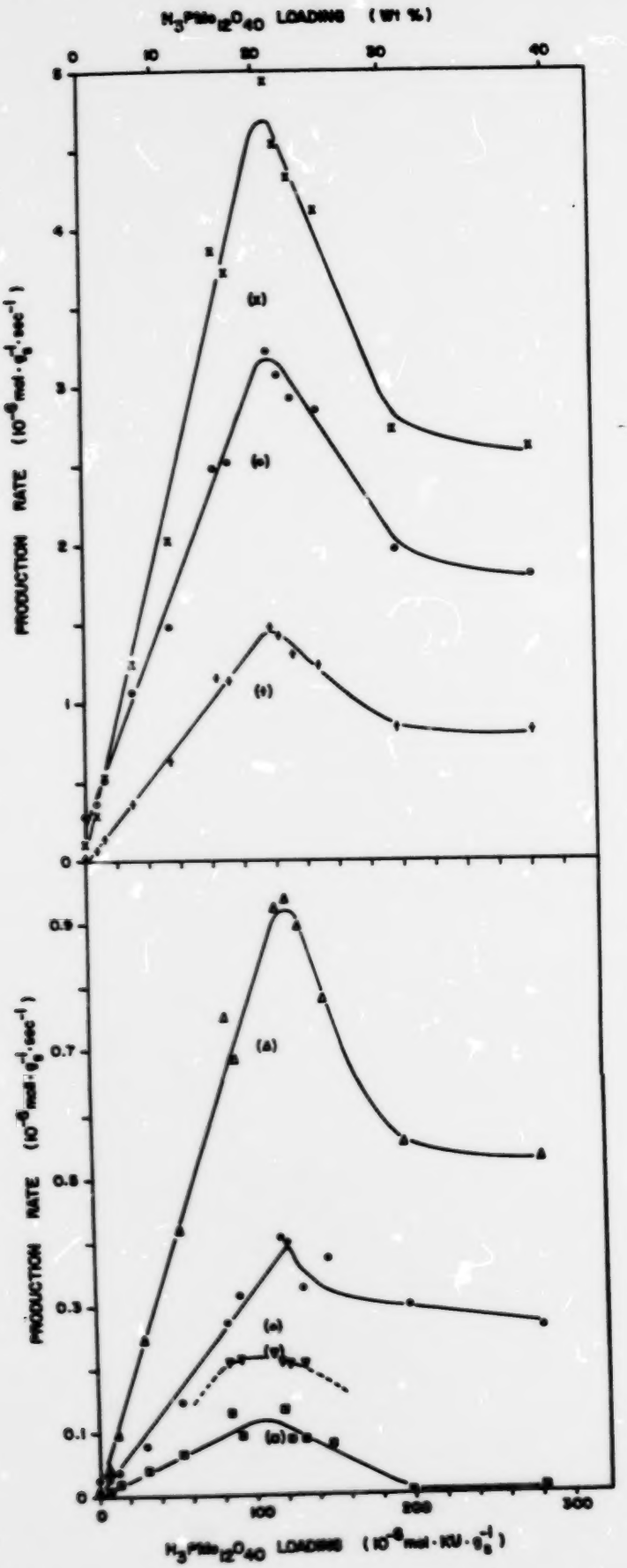
Figure 5: Infrared spectra of acetonitrile solution after washing of the following supported HPMo samples calcined in different conditions.

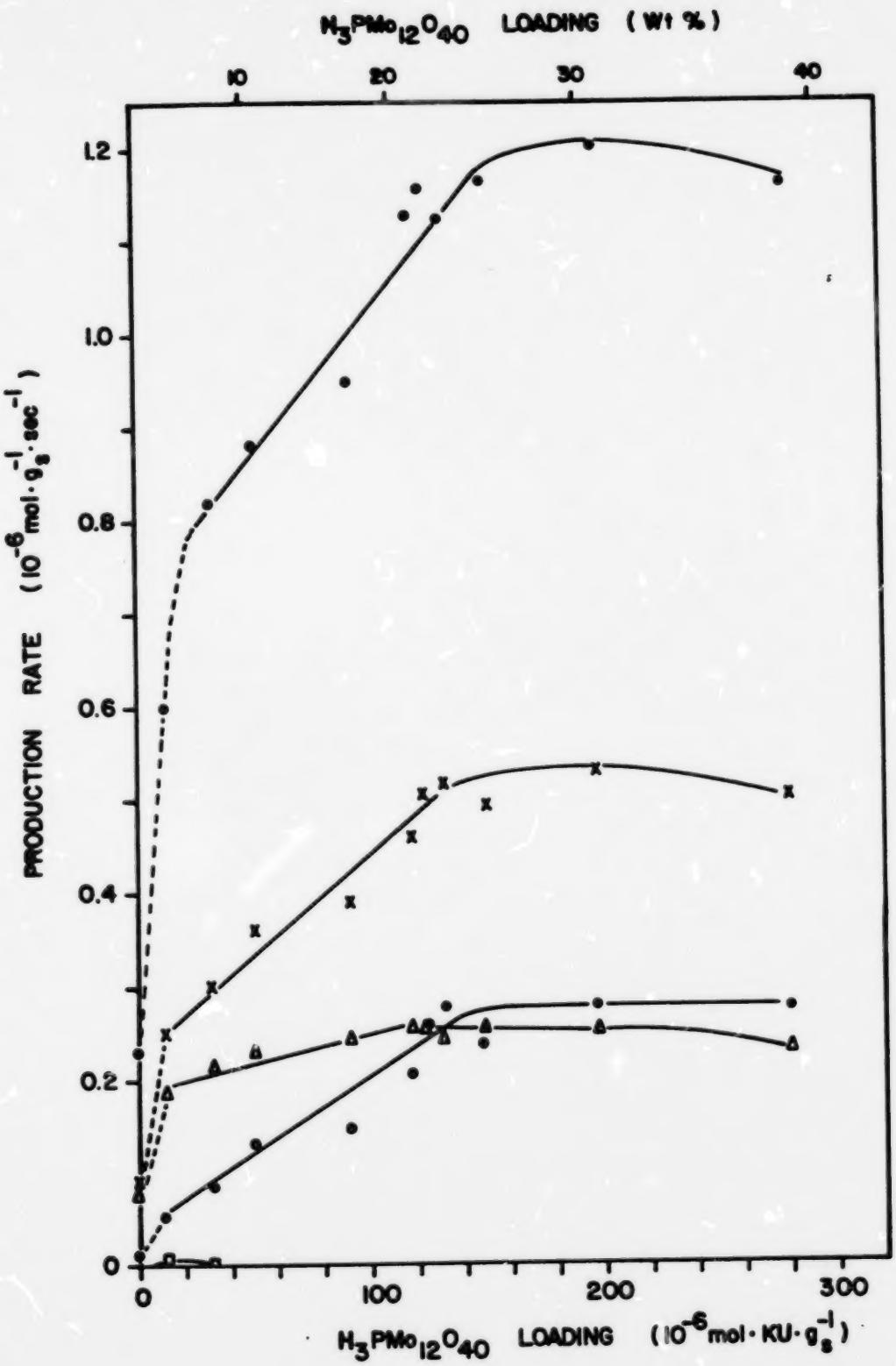
a) 1.16 HPMo, 350°C, 2h., b) 11.1 HPMo, 350°C, 2h., then 20.1 HPMo sample c) 350°C, 16h., d) 450°C, 16h, e) 550°C, 16h, f) 640°C, 16h., g) 640°C, 16 h., followed by a test at 570°C, 10h., h) 730°C, 16h.. The positions of the bands of the bulk $H_3PMo_{12}O_{40}$ are reported at the bottom of the figure.

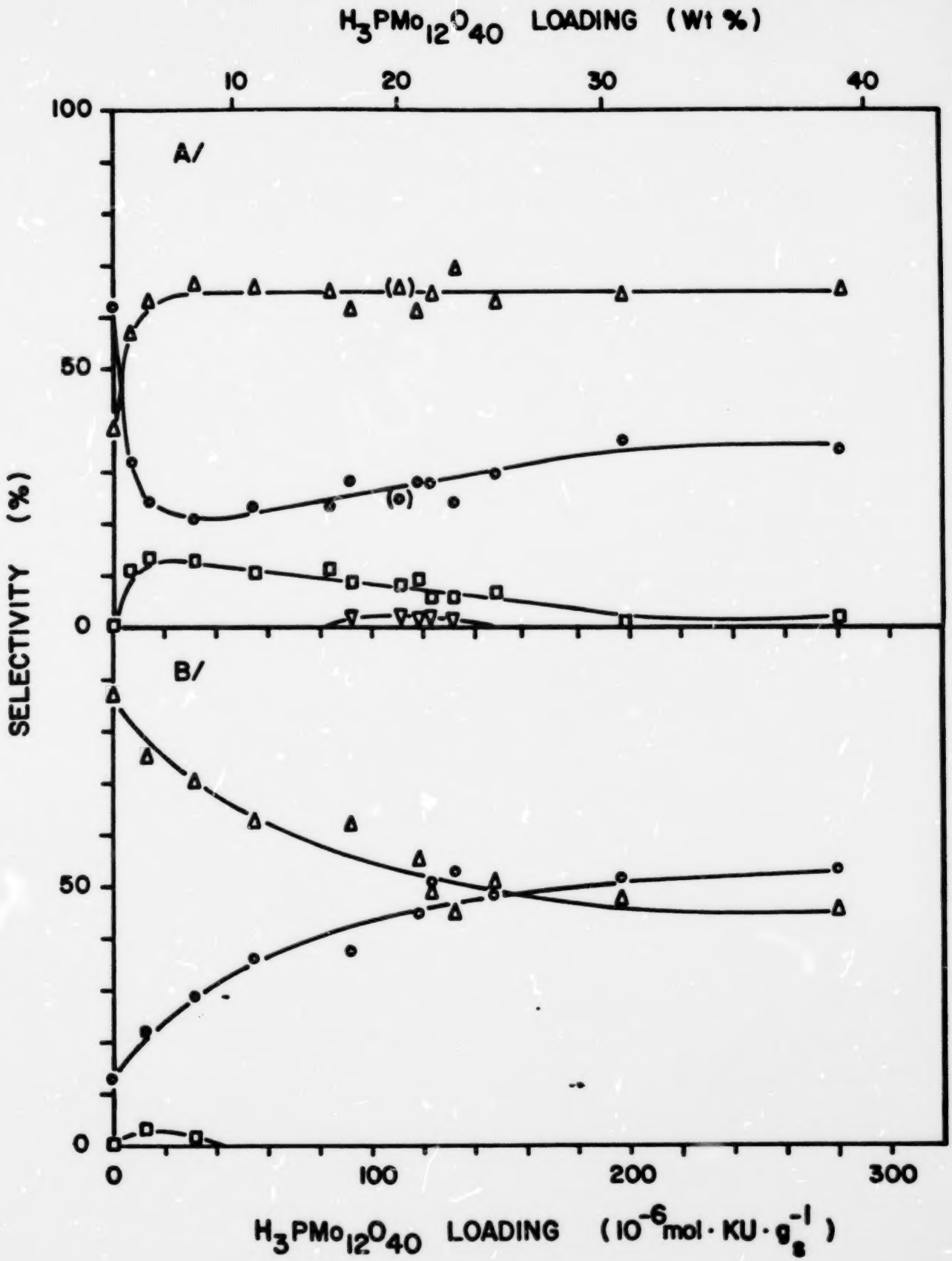
Figure 6: Infrared photoacoustic spectra of the bulk 12-Molybdosphosphoric acid treated at different temperaturesin vacuum or CH_4 + N_2O atmosphere.

a) 530°C (N_2O + CH_4), b) 450°C (N_2O + CH_4)
c) 550°C (vac), d) 450°C (vac), e) 350°C (vac),
f) 210°C (vac), g) 25°C (air).

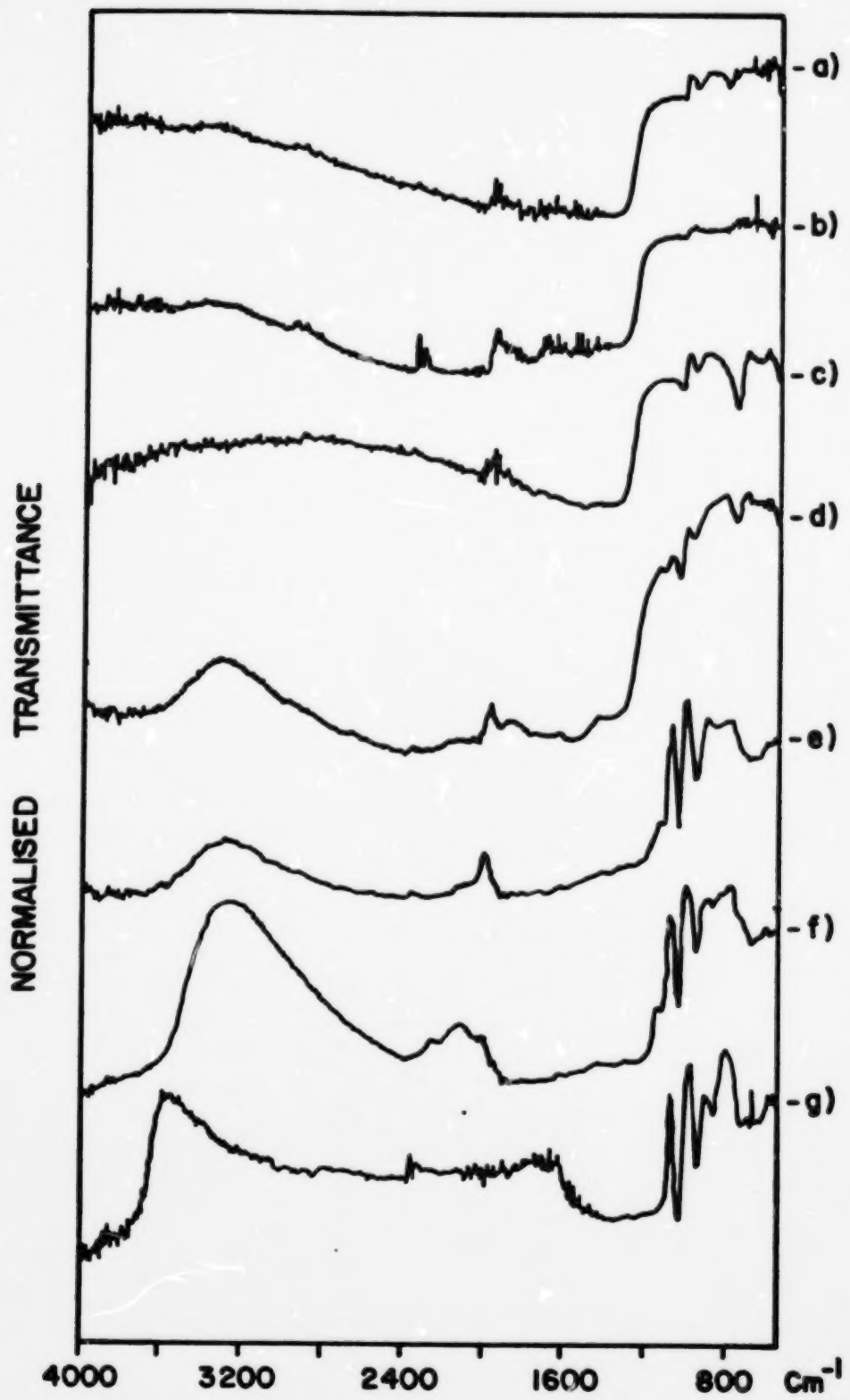

A/
C/
B/
D/
SELECTIVITY (%)
100
50
0
SiO_2
CH_4 CONVERSION (%)
5
3
2
1
0
SiO_2
SAMPLE LOADING (Wt % Mo)
20
10
0
600
800
1000
CALCINATION TEMPERATURE (K)
0
20
40
60
80
100
TIME OF CALCINATION (hours)


$H_3PMo_{12}O_{40}$ LOADING (wt %)
PRODUCTION RATE (10^{-8} mol · g_s^{-1} · sec^{-1})
(x)
(o)
(•)
(Δ)
(▽)
(□)
$H_3PMo_{12}O_{40}$ LOADING (10^{-8} mol · KU · g_s^{-1})


$H_3PMo_{12}O_{40}$ LOADING (Wt %)
10
20
30
40
1.2
1.0
0.8
0.6
0.4
0.2
0
PRODUCTION RATE (10^{-6} mol · g_s^{-1} · sec^{-1})
0
100
200
300
$H_3PMo_{12}O_{40}$ LOADING (10^{-6} mol · KU · g_s^{-1})


$H_3PMo_{12}O_{40}$ LOADING (Wt %)
10
20
30
40
100
A/
50
0
SELECTIVITY (%)
(Δ)
(o)
B/
50
0
0
100
200
300
$H_3PMo_{12}O_{40}$ LOADING (10^{-6} mol · KU · g_s^{-1})

i
h
g
f
e
d
c
b
a
1063
969
883
960
819
1200
1000
800
Cm-1
I.R. ABSORBANCE


NORMALISED TRANSMITTANCE
a)
b)
c)
d)
e)
f)
g)
4000
3200
2400
1600
800
Cm⁻¹

THE OXIDATION OF METHANE ON HETEROPOLYOXOMETALATES. III. EFFECT OF THE ADDITION OF CESIUM ON SILICA-SUPPORTED 12-MOLYBDOPHOSPHORIC ACID, MOLYBDENA, VANADIA, and IRON OXIDE

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ABSTRACT

The effect, on the oxidation of methane with nitrous oxide, of the addition of cesium to silica-supported 12-molybdophosphoric acid (HPMo), molybdena, vanadia, and iron oxide has been studied. All four catalytic systems show similarities in results with cesium producing a poisoning effect, eventually reducing the solid to a behaviour similar to that of the support. The correspondence of deactivation with the number of available protons in supported HPMo suggests that the protons play a crucial role in the oxidation process. A mechanism is postulated in which the protons abstract oxygen atoms to produce anionic oxygen vacancies which are visualized as vital to the oxidation process on HPMo. The similarity of behaviour of silica-supported molybdena, vanadia, and iron oxide to that of HPMo on addition of cesium suggests the existence of isopoly oxometalate structures on these catalysts. The similarity of experimental cesium saturation values with those for hydrogen expected from a postulated stoichiometry for such structures provides support for such conclusions.

INTRODUCTION

Previous work from this laboratory (1) has shown that the silica-supported heteropoly oxometalates with Keggin structure, for example, 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiMo), and 10-molybdo-2-vanadophosphoric acid are effective catalysts for the partial oxidation of methane by nitrous oxide in the temperature range from 793 to 843 K. In contrast, the tungsten-based heteropolyoxometalate, 12-tungstophosphoric acid (HPW) and 12-tungstosilicic acid (HSiW) were found to be relatively inactive in such a process. Further work (2) on HPMo supported on silica provided evidence strongly suggesting that the Keggin Unit (KU) $PMo_{12}O_{40}^{3-}$ fixed on the support is the species primarily responsible for the activity and selectivity of the catalyst. In addition it was shown that severe pretreatment conditions, such as calcination in air at 640°C for 16 hours or 550°C for 40 hours, together with a catalytic reaction at 570°C for 10 hours were not sufficient to destroy all the Keggin Units. However, almost complete thermal degradation occurred after calcination at 730°C for 16 hours in air. This remarkable structural stability of the heteropoly anion is apparently due to an advantageous interaction between the support and the Keggin Unit, the latter being dispersed as isolated species grafted on the support surface, up to a loading of 120 micromoles KU per gram of support (0.1 KU cm^{-2}). (2).

The heteropoly acids are known to contain exchangeable protons (3-9), a property suitable for the preparation of a variety of salts. The surface and catalytic properties of the salts of a number of heteropoly acids have been studied (10-19), in particular those of 12-molybdophosphoric acid for oxidation (10,11), acid-catalyzed reactions (12,13) or redox processes (11,14). The

monovalent salts, and particularly those containing alkaline element cations appear to have been more extensively studied. In particular, it has been shown that partially saturated cesium salts of bulk 12-molybdophosphoric acid had an increased activity in the partial oxidation of butane (15,16). However, such activity enhancement was coincident with an increase in specific surface area. In this laboratory the structural properties of the monovalent salts of 12-molybdo- and 12-tungsto-phosphoric acids have been studied (4-9,17-19), and the importance of cation size in structural microporosity and secondary bulk structure has been shown. With the aforementioned anions, a cation size in the range 2.5- 3.5A (Cs^+, NH_4^+, K^+) produced a maximum in micropore volume and surface area.

Since each KU of the silica-supported HPMo catalyst is evidently isolated on the support surface, the supported heteropoly acids may be viewed as a system free of bulk structure. Thus it appeared possible to study the effect of the exchange of hydrogen by cesium without the intrusion of surface area effects. The present work examines the effect produced by cesium on both supported heteropoly oxometalates and other partial oxidation catalysts such as supported oxides of molybdenum, vanadium, and iron.

EXPERIMENTAL

Catalysts

The method of preparation of the silica-supported 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiW) and 10-molybdo-2-vanadophosphoric (HPV_2Mo_{10}) acids has been described previously (1,2). These acids were loaded on the silica support (Grace-Davison, grade 407, 740 $m^2\ g^{-1}$) to provide 0.068 Keggin Unit (KU) per nm^2 of support surface (or 84 micromole KU per gram of support), corresponding to loading of 16.0, 16.0, 21.2, 21.2, and 16.2 wt % of HPMo, HSiMo, HPW, HSiW and HPV_2Mo_{10}, 30 H_2O, respectively.

The supported cesium salts of these heteropoly acids were prepared by the impregnation of the calcined supported heteropoly acids with an excess of an aqueous solution of cesium carbonate (Alpha Products 99.9%) acidified with 1 M nitric acid. After evaporation to dryness at 80°C the solids were calcined at 200°C for one hour. No significant quantities of precipitate were produced in the application of this technique to HPMo, HSiMo, and HPV_2Mo_{10} catalysts but precipitation did occur with HPW and HSiW catalysts. Amounts of cesium carbonate to yield 0 to 8 atoms of cesium per KU have been added, and the resulting catalysts are labelled as x CsPMo, where x represents the number of cesium atoms per HPMo KU.

The preparation of the 3 wt % Mo/SiO_2 and 1.66 wt % V/SiO_2 catalysts has been described previously (2). The 1.82 wt % Fe/SiO_2 catalysts were prepared by impregnation of the silica with an excess of an iron oxalate aqueous solution, evaporation to dryness in air at 80°C and calcination in air at 200°C for two

hours. The three supported metal catalysts were prepared to contain 0.27 atom of metal per gram of support surface (332 micromol. metal per gram of support).

Deposition of cesium on the supported oxides (0-1.5 Cs per atom of metal) was accomplished in a manner similar to that with the supported heteropoly oxometalates and is labelled as xCsM, where x and M represent the number of cesium atoms per M atoms of supported metal oxide (M = Mo, V, Fe). A sample containing 0.24 atoms of cesium per nm^2 was also prepared by impregnation of cesium carbonate, drying, and calcination in air at 200°C for two hours.

Catalytic Experiments

The reactor, analytical systems and operating conditions have been described previously (1,2). In the present work one set of operating conditions was primarily employed: reaction temperature, T_R = 843 K, catalyst mass W = 0.5 g, total flow rate F = 30 ml min^{-1}, feed composition, CH_4 (67 mol %), N_2O (33 mol %).

The catalyst samples were pretreated in helium for one hour at the reaction temperature to remove water. The reaction was allowed to proceed for three hours to guarantee the attainment of steady state prior to any measurements. The turnover number is calculated per KU for the heteropoly acids or per atom of metal for the supported oxides. Selectivities are reported as mol % CO, CO_2, CH_2O and CH_3OH produced.

The xCsPMo samples were reduced in hydrogen at 843 K for one hour prior to reactions being performed. After a purge with hydrogen two ml pulses of N_2O were injected and the amount of nitrogen measured. This sequence was performed two times in succession on each catalyst sample. The amount of nitrogen

produced is equivalent to the number of oxygen atoms consumed in the reoxidation since no oxygen was produced. Fifteen such pulses were required to reoxidize the solid. For comparative purposes a similar experiment was also performed on silica.

Apparent activation energies have been calculated from the results of 5 to 6 experiments performed randomly in the temperature range 773 - 863 K. In all cases, except that of silica where a discontinuity was found at 820 K as previously reported (1), a good linearity of the Arrhenius plots was found.

RESULTS

The effect of the amount of cesium on the activity and selectivity of the supported HPMo, HPW, HSiMo, HPV_2Mo_{10} for the $CH_4 + N_2O$ reaction is reported in Figures 1 and 2. The turnover rates of both methane and nitrous oxide decrease approximately linearly as the amount of cesium is increased up to approximately 2 cations per KU. With further increase of the latter the two turnover numbers decrease more precipitously until small values, approximately equivalent to those found for the silica support, are reached when 3.5 to 4 cations per KU are present. Semiquantitatively similar changes may be observed with the selectivities. Small changes are observed up to approximately 2 cations per KU while more substantial changes occur between 2 and 4 Cs/KU until values similar to those for the silica support are reached. Evidently the catalytic properties of the supported HPMo species have been completely poisoned by the addition of 3.5 to 3.8 Cs per KU, a value similar to the 3 H possessed by each KU in the bulk stoichiometric acidic form.

The activities of the HSiMo and HPV_2Mo_{10} acids are completely poisoned and that of HPW is nearly completely poisoned by the addition of cesium (Fig. 2). However the shapes of the turnover number curves differ from that found with HPMo. With the former catalysts the turnover number decreases monotonically with increase in the cesium content, reaching values expected for the support for amounts of cesium/KU as small as 2 for HSiMo and HPW, but approximately 4 with HPV_2Mo_{10}. Observations during the preparation of these different catalysts may be relevant to these results. It has been noted that a precipitate is formed when cesium carbonate is added to the supported HPW and HSiW catalyst

while with the HSiMo and HPV_2Mo_{10} samples no precipitate was observed during the impregnation. With the former catalysts the precipitous decrease in activity may, at least in part, be due to the destruction of the Keggin structure or aggregation of the smaller clusters into larger particles during the impregnation with the cesium carbonate solution. Both the HSiMo and HPV_2Mo_{10} are known to be considerably less stable then HPMo. In addition, the aqueous solution of cesium carbonate tends to neutralize the solution which may be detrimental to the stability of the anionic structure of HSiMo and HPV_2Mo_{10}. However, it is apparent from Figure 2 that whatever decomposition products may be generated, if any, such substances are either inactive or are themselves poisoned by the cesium since both the activity and selectivity approach that of the support with increase in the amount of cesium/KU.

The changes in product composition with addition of cesium can also be seen in Figure 2. With silica-supported HPV_2Mo_{10} the product composition is unchanged after addition of one Cs/KU but with further addition of cesium the proportion of carbon dioxide increases while that of carbon monoxide and formaldehyde decreases, approaching that of silica after addition of four Cs/KU. HSiMo exhibits similar behaviour although the product composition resembles that found with silica after the addition of one Cs/KU. In contrast, with HPW the product composition changes but does not approach that of the support.

Aggregation of the active KU into larger particles may also result in a decrease in activity. As alkanes are unable to penetrate into the bulk of the heteropoly compounds, and consequently reaction of such molecules is confined to the surface of the heteropoly compounds, an aggregation would result

in the availablity of a reduced number of active sites and an activity and selectivity presumably different from that of the support.

Further investigation of the poisoning by cesium of the activity of the supported HPMo has been undertaken. A study of the reoxidation of samples prereduced by hydrogen was expected to provide information on the poisoning effect when a more powerful reducing agent is used. After reduction by hydrogen at 570°C for one hour the amount of oxygen necessary to reoxidize the sample was determined by the injection of 15 successive pulses of nitrous oxide and the measurement of the total amount of nitrogen produced. The effect of the amount of cesium on the amount of oxygen consumed may be seen in Fig. 3b. A linear decrease is observed in the number of oxygen per KU necessary to reoxidize the sample as the cesium is increased to approximately three Cs/KU. With additional increases of cesium no further change is evident. It may be seen from Fig. 3b that 19 oxygen atoms per KU are required to reoxidize the reduced HPMo, with no cesium present, but this decreases to approximately four oxygen per KU on addition of cesium.

The addition of cesium also reduces the apparent activation energy of the $CH_4 + N_2O$ reaction (Fig. 3a). For amounts of cesium up to approximately two cations/KU the activation energy is unchanged at 32±2 Kcal mol^{-1}. Additional increases in the cesium content reduce the activation energy to 12±2 Kcal mol^{-1} at approximately 4 Cs/KU, a value similar to that for the silica support itself.

The ion exchange properties of the heteropoly acids are well known and used extensively for the preparation of numerous salts. Since HPMo contains three protons per KU, a saturation close to three cesium cations per KU was anticipated, provided that other phenomena such as aggregation or decomposition

of the KU, or significant adsorption capacity of the support do no interfere. Since, in the case of the Mo, V and Fe supported oxides the ion exchange capabilities and the number of exchangeable protons are not known, the doping by cesium may provide valuable information.

Both the Mo/SiO_2 and V/SiO_2 catalysts are known to catalyze the partial oxidation of methane (20-22). In the present work the supported iron on silica has been found more active for the conversion of methane than either Mo/SiO_2 or V/SiO_2, although the selectivities are different (Figs. 4-6). The Fe/SiO_2 catalyst produces mainly CO_2 (68%) and CO (30%) with little formaldehyde (≈0.5%) while 2% of methanol is produced.

The effect of the amount of cesium on the conversion and selectivity for the $CH_4 + N_2O$ reaction on Mo, V and Fe catalysts is also shown in Figures 4-6. Similarly to that found with the HPMo catalysts, the graphs of activity for various amounts of cesium exhibit three distinct types of behaviour. Both the vanadium and iron catalysts, which are very active catalysts without cesium, yield curves similar to that found with HPMo. However, in contrast to the observations with the latter, after addition of an amount of cesium sufficient to produce no further changes in activity, the vanadium and iron catalysts have residual activities greater than that of the support itself. It is also evident from the figures that a similar comment applies to the selectivity.

For the Mo/SiO_2 catalyst, which has a low activity in the absence of cesium, small quantities of cesium lead to an initial increase in activity, followed by a decrease, and as with the vanadium and iron catalysts, ultimately an activity level higher than that of the support. The selectivity also fails to reproduce that of the support. In contrast with the results for HPMo,

vanadium and iron catalysts, cesium appears to act as an effective promoter in amounts up to approximately 0.4 Cs/KU.

With the Mo, V and Fe catalysts the selectivity is altered to favour methanol and carbon dioxide as cesium is added, while the quantities of carbon monoxide and formaldehyde decrease and in the latter case become negligibly small.

DISCUSSION

The effect of the amount of cesium on different supported catalysts provides both structural and catalytic information on these systems. Structurally, the observation that a saturation level is reached can be used to determine the number of exchangable protons in the system. Since with the HPMo catalyst, three protons are present per Keggin Unit, provided that the Keggin Units are still present in the sample, the saturation should be reached at 3Cs/KU. The present results show a limit at 3.5 Cs/KU. The difference may be attributed to the difficulty in completely exchanging all protons with cesium ions, so that a slight excess is required for that purpose. Since the addition of cesium to silica has no significant effect on the catalytic properties of the support, the measured changes in activity can be referred to hypothetical lines drawn to intersect the activity of the support at three Cs/KU (Fig. 1b). Although, at sufficiently high temperatures the presence of products of decomposition of the Keggin structures may play a role in fixing some cesium ions, the similarity of the measured saturation value to that expected provides additional evidence that Keggin structures are held on the support, as proposed previously (2).

The addition of cesium also produces substantial changes on the supported oxides of Mo, V and Fe. Fe and V are poisoned similarly to that observed with HPMo while the Mo system shows an initial increase of activity. It will be proposed, however, that such observations are consistent with the same effect of cesium, the difference in the observations with Mo/SiO_2 being attributable to its small initial activity. The number of H^+ per atom of metal has been reported in Table 1 and compared to the value of that quantity that would be

expected if isopoly oxometalate structures are present on the support and are the active species for the CH_4 oxidation. Interestingly, the experimental values are similar to those calculated from known isopoly anions. The heptamolybdate anion is a commonly encountered species in aqueous solution and, as proposed for the Mo/Al_2O_3 catalyst, at least in an intermediate range of loading (23), could also be the predominant species on the silica support. With the V/SiO_2 catalyst, the values calculated by assuming the presence of the anions $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ closely approximate those from experiment. With iron, the results suggest the existence of a polyoxometalate structure with 0.21 H^+/Fe or approximately 5 Fe per H^+. Whatever the precise structure of the surface species in these systems it is important to recognize here the strong analogy between the $HPMo/SiO_2$ and supported oxide catalysts.

With the $HPMo/SiO_2$ catalyst the results undoubtedly show that the exchange of all the protons by the cesium is at the origin of the complete poisoning of the CH_4 oxidation process. This demonstrates that the proton has an important role in the oxidation process. Although it could be claimed that the proton is the reactive species activating the methane molecule to produce a carbocation

$$CH_4 + H^+ \rightarrow CH_5^+$$

there is considerable evidence that the O^- species is the reacting species which extracts a hydrogen to generate a methyl radical (24)

$$CH_4 + O^- \rightarrow OH^- + CH_3\cdot \qquad (1)$$

It can therefore be proposed that protons are required in the oxidation of CH_4 on HPMo to provide for the creation of vacancies by the removal of water as

$$2\ KUOH \rightarrow KUO + KU\square + H_2O \qquad (2)$$

Subsequently N_2O can decompose on these vacancies

$$N_2O + KU\square \rightarrow N_2 + KUO^* \quad (3)$$

and an O^- ion can be generated

$$KUO^* \rightarrow KU^+ O^- \quad (4)$$

As can be readily understood, substitution of protons by cesium blocks the dehydration reaction (2) and consequently the subsequent reactions are also terminated. Since complete poisoning can apparently be achieved it can be concluded that the chain of reactions 2-4 is the only source of O^- ions in the $HPMo/SiO_2$ catalyst. Moreover this demonstrates that only the oxygen (presumably held in the peripheral sites of the heteropoly anion) originating from the N_2O decomposition is active for the methane activation while the remaining structural oxygen of the heteropolyanions does not participate in the activation process.

As can be deduced from reaction 2, the generation of one vacancy results from the loss of two protons. Therefore the number of vacancies that can be created is half the number of cesium (or H^+), that is 1.5 per KU. Obviously such a value should be understood as implying that one-half of the anions with Keggin structure have one vacancy each while the other half have two vacancies per anion. In the case of $H_4SiMo_{12}O_{40}$ a complete dehydration should produce two vacancies on every anion. This number of vacancies will define the number of O^- species which can be considered as sites of the reaction. Earlier work from this laboratory (5,7-9) on the temperature programmed desorption of water from heteropoly oxometalates showed that the water which desorbed from the heteropoly acids at high temperatures resulted from the protons stripping oxygen from the Keggin Units. With $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ the equivalent of 1.5 (±0.1) water molecules per KU were measured with $H_4SiW_{12}O_{40}$.

The initial effect of the cesium appears therefore to be inhibiting the regeneration of the O^- species by blocking the dehydration reaction 2. However this effect alone should presumably produce a linear decrease in the activity (such as that shown by the dotted line in Fig. 1b). The discontinuity in the experimental data at 2.2 Cs/KU demonstrates that a second effect of the cesium is extant. Tentatively, it is suggested that such an additional effect may be electronic in nature since cesium, being very electropositive, may perturb the electron density distribution in the Keggin Unit and therefore also in the sites still free (i.e. not blocked by Cs). Since the remaining sites appear to be more active than expected, the effect of this perturbation is apparently advantageous. The maximum deviation from a purely poisoning relationship can be expected at 2Cs per KU since for that value only one site (vacancy) can still be generated by a dehydration (reaction 2) on a Keggin Unit while being under the influence of two cesium ions. It is evident from Fig. 1 that the discontinuity occurs at approximately 2.2 Cs/KU, a value in good agreement with that expected from the aforementioned theoretical considerations. The activity at 2.2 Cs/KU may be estimated as approximately double that which would be expected for a purely poisoning phenomenon, a value which clearly demonstrates a substantial effect.

As can be observed in figure 3a, this electronic effect has little or no influence on the activation energy, the increase in rate being apparently related to a change in the preexponential factor. This is also consistent with a retention of the original mechanism since the selectivity in the 0-2 Cs/KU range is relatively constant. Since the reaction of the O^- species with CH_4 (reaction 1) has been shown to occur readily even at very low temperatures (24),

it is therefore probable that one of the reactions 2-4 is the rate determining step which is influenced by the cesium. Although Lunsford (20) has proposed that the dehydration step (reaction 2) may be the energy consuming process, it is possible that, in the present system, the electron transfer process (section 4) is rate limiting, while the N_2O decomposition step is presumably facile.

The similarity of the effect of cesium with the Mo, V and Fe catalysts and the HPMo catalyst is readily apparent. However, with the supported oxides the activity is not completely eliminated by the addition of cesium but reaches a plateau which in the case of the Mo catalyst is higher than that of the initial catalyst activity. In addition, the selectivities which accompany the activities at their plateau do not reproduce that of the support. This suggests that an oxidation process on the supported oxide may still be occurring, presumably by a mechanism different from that with the HPMo catalyst, even after exchange of all exchangable protons. It may be recalled that three types of oxygen exist in the heteropoly oxometalate anions with Keggin structure. One of these bridges the central atom of the anion and the peripheral metal atoms while a second interconnects two of the latter atoms. The third type is attached to the peripheral metal atoms and protrudes from the anion. It is the latter type which is directly associated with any protons present and which is removed to form vacancies. While both the heteropoly - and the isopoly oxometalate structures possess oxygen atoms less directly associated with protons it appears that in the latter species, and under the influence of cesium, these oxygens may be capable of conversion to species appropriate for the oxidation process.

It is however, conceivable that nonexchangeable protons may remain after introduction of saturation quantities of cesium. It may be relevant in this context to note that, in the three supported oxide systems the selectivity to methanol increases while that to formaldehyde decreases with increasing quantities of cesium. This may be related to the elimination of protons which could be involved in acid-catalyzed methanol conversion processes. Thus, in the case of the supported molybdenum oxide catalyst, the use of cesium as an additive may increase the activity and enhance the production of methanol.

While postulated reactions 1-4 are important steps in the catalytic oxidation process, they obviously represent only a part of the overall mechanism which presumably requires the generation of the methyl radical. While the O^- species involved in these reaction steps is apparently responsible for the abstraction of a hydrogen from the methane molecule it is not necessarily directly involved in the oxidation process itself. The subsequent reaction of the methyl radical with other oxygen species will more probably determine the selective or nonselective path that is followed. Haber et al (25) have proposed that reaction of the radical with O^- species will result in complete oxidation whereas that with an $O^=$ species will lead to partial oxidation products. As noted previously both types of oxygen are present in heteropoly - and isopolyoxometalate anions and can evidently play important roles in both oxidation processes.

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TABLE 1: Comparison of the experimental and hypothetical amount of protons per atom of metal formed by cesium exchange.

Catalyst	Experimental cesium Saturation ratio (Cs/atom metal)	Possible polyoxo-metalate species	Theoretical saturation ratio (H^+/atom metal)
$HPMo/SiO_2$	0.29 (3.5 Cs/KU)	$PMo_{12}O_{40}^{3-}$	3/12 = 0.25
Mo/SiO_2	0.95	$Mo_7O_{24}^{6-}$	6/7 = 0.86
V/SiO_2	0.47	$HV_{10}O_{28}^{5-}$	5/10 = 0.50
		$H_2V_{10}O_{28}^{4-}$	4/10 = 0.40
Fe/SiO_2	0.21	---	---

FIGURE CAPTIONS

Figure 1: Turnover rate and selectivity of the CH_4 oxidation by N_2O versus the amount of cesium on the 16 wt% HPMo Catalyst.
Reaction Conditions: T_R = 843 K, W = 0.5 g, F = 30 $mLmin^{-1}$
CH_4 (67% mol) N_2O (33%)
Symbols: (Δ) CO, (o) CO_2, (□) CH_2O, (x) N_2O turnover rate, (•) CH_4 turnover rate.
(Dotted lines are hypothetical curves.)

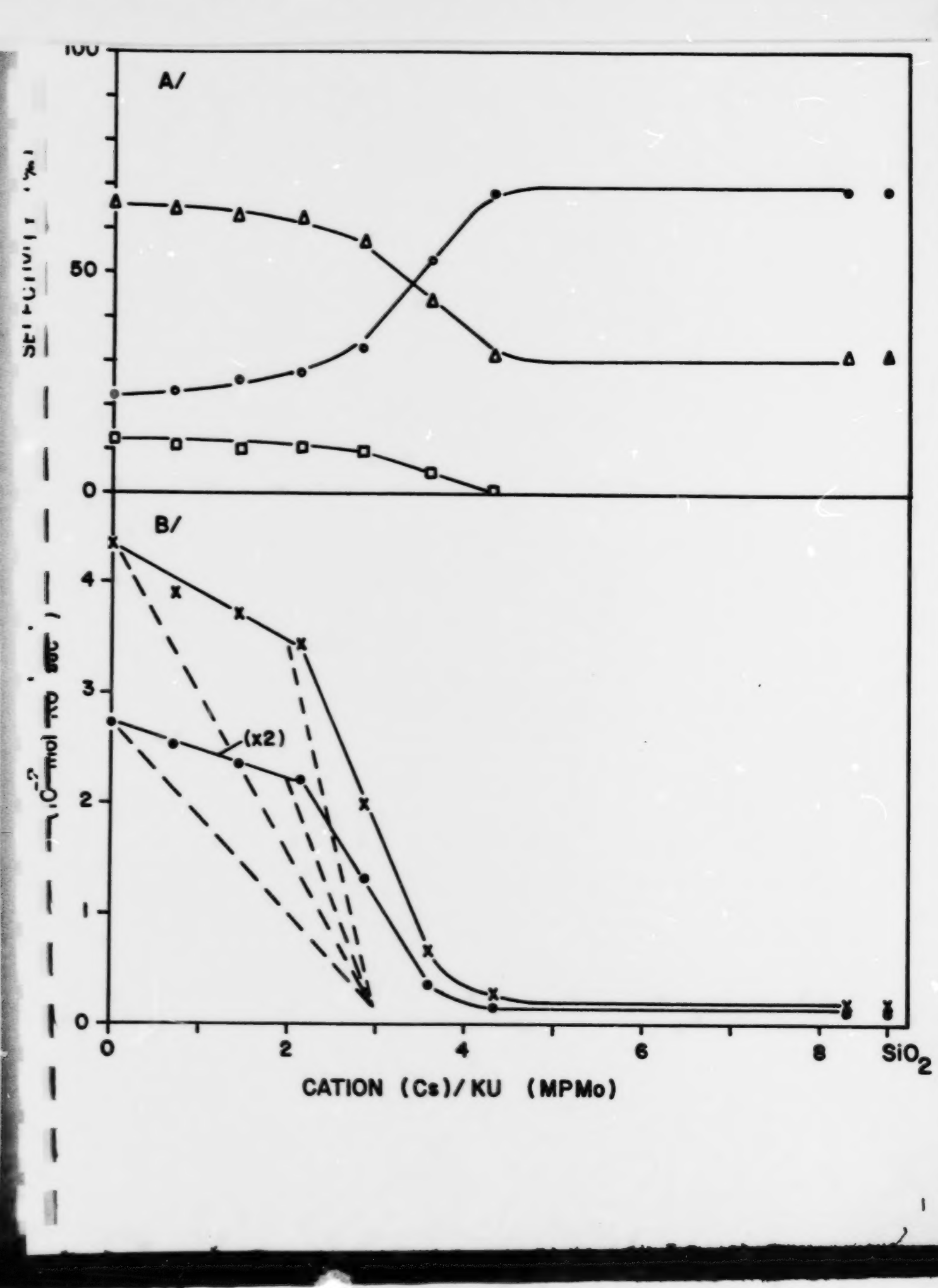
Figure 2: Turnover rate and selectivity of the CH_4 oxidation by N_2O vs the amount of cesium on the 16.2 wt% HPV_2Mo_{10}, 16 wt% HSiMo and 21.2 wt % HPW.
Same reaction conditions as figure 1. Symbols: (Δ) CO, (o) CO_2, (□) CH_2O, turnover rate: (x) HPV_2Mo_{10}, (•) HSiMo, (▲) HPW.

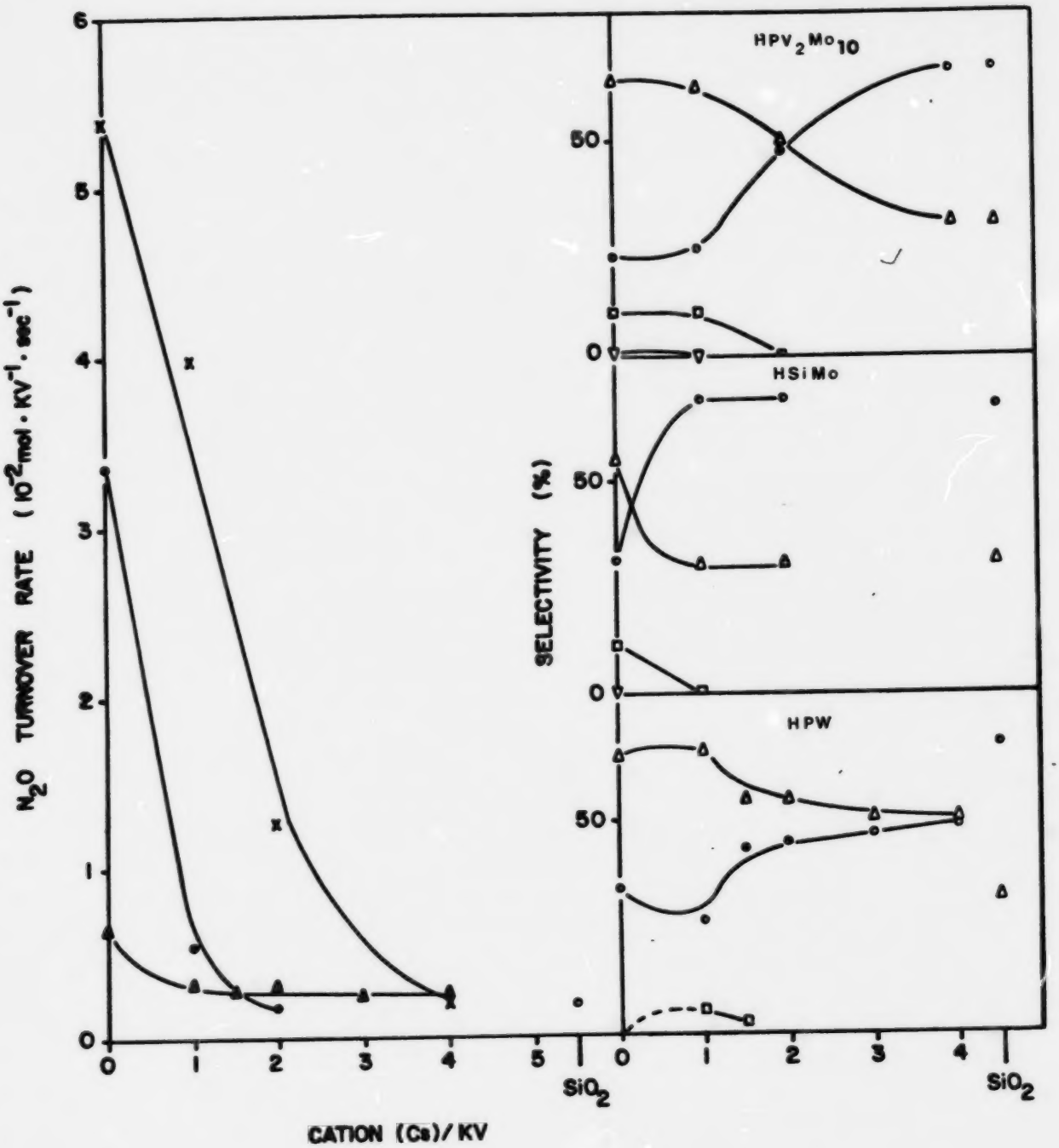
Figure 3: Variation of A/ the apparent activation energy and B/ the amount of oxygen consumed for reoxidation after H_2 reduction at 843 K for 1 hour, versus the amount of cesium on the 16 wt% HPMo. Reaction conditions for A: W = 0.5 g, F = 30 $mLmin^{-1}$, CH_4 (67%), N_2O (33%), Symbols: (•) first measure, (o) second measure.

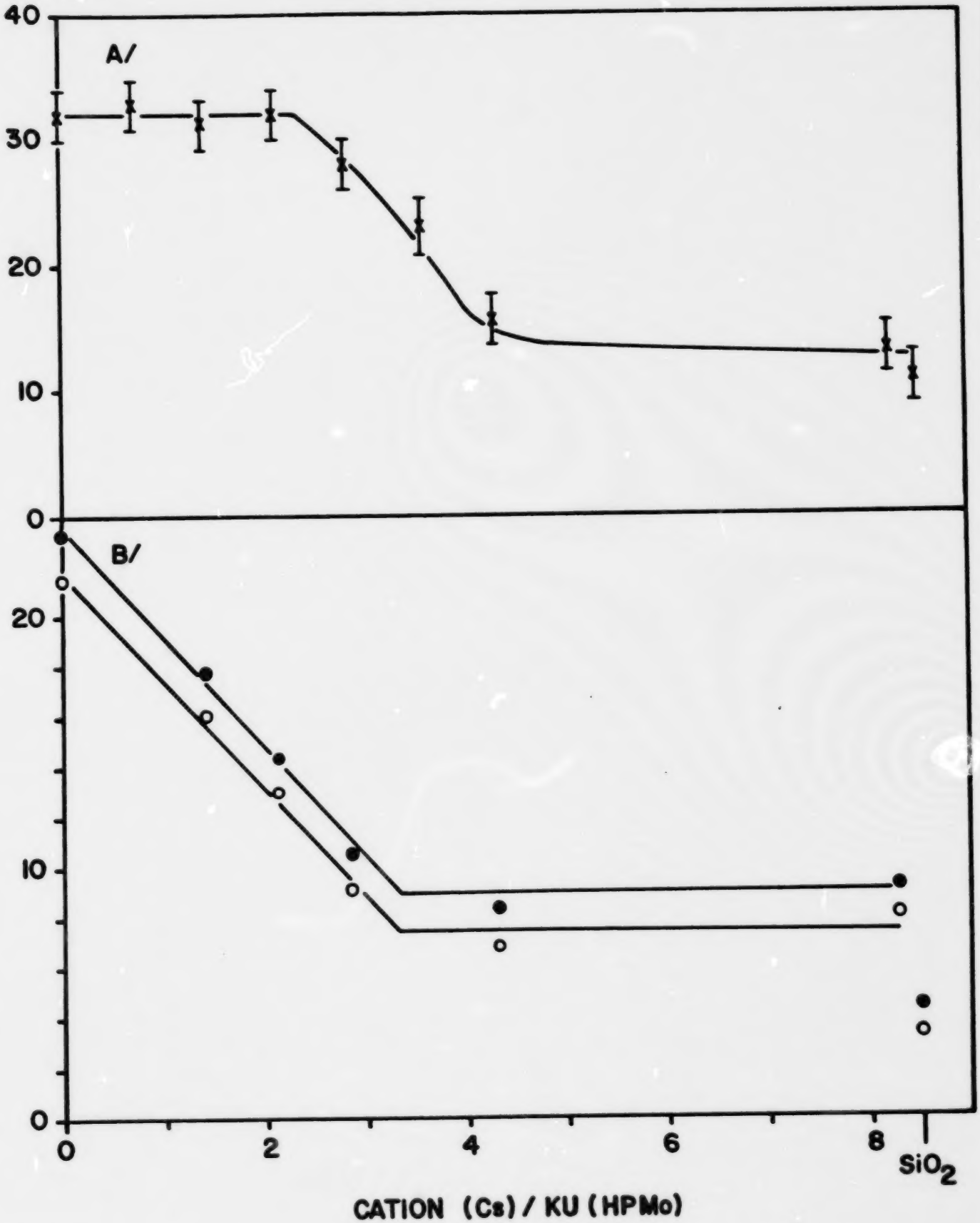
Figure 4: Turnover rate and selectivity of the CH_4 + N_2O reaction versus the amount of cesium on the 3 wt% Mo/SiO_2 catalyst. Reaction conditions: T_R = 843 K, W = 0.5 g, F = 30 $mLmin^{-1}$, CH_4 (67%) N_2O (33%). Symbols: (Δ) CO, (o) CO_2, (□) CH_2O (▽) CH_3OH, turnover rate: (x) samples prepared with cesium nitrate and (+) with cesium carbonate.

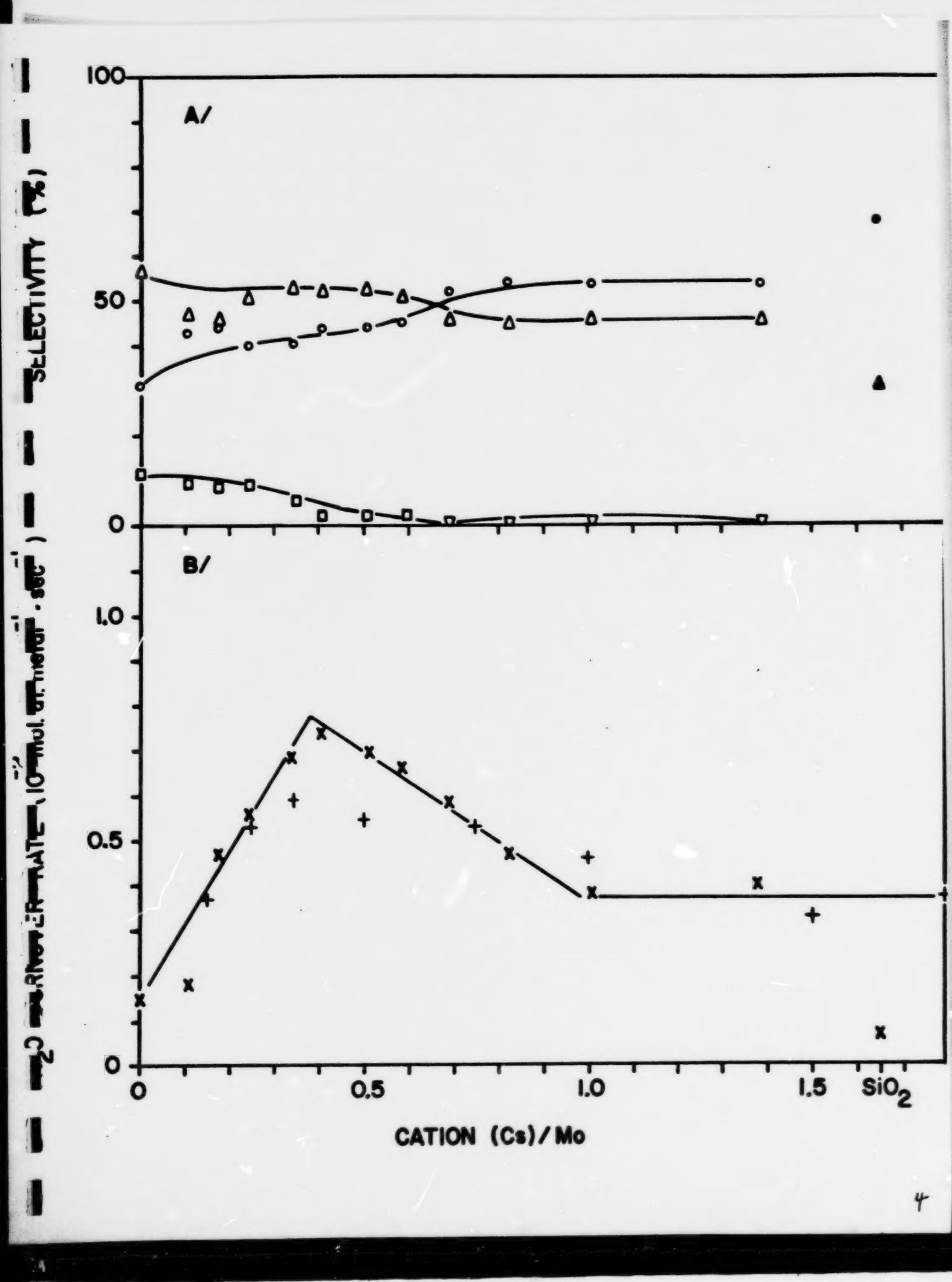
Figure 5: Turnover rate and selectivity of CH_4 oxidation by N_2O versus the amount of cesium on the 1.66 wt% V/SiO_2 catalyst. Same reaction conditions and symbols as figure 4.

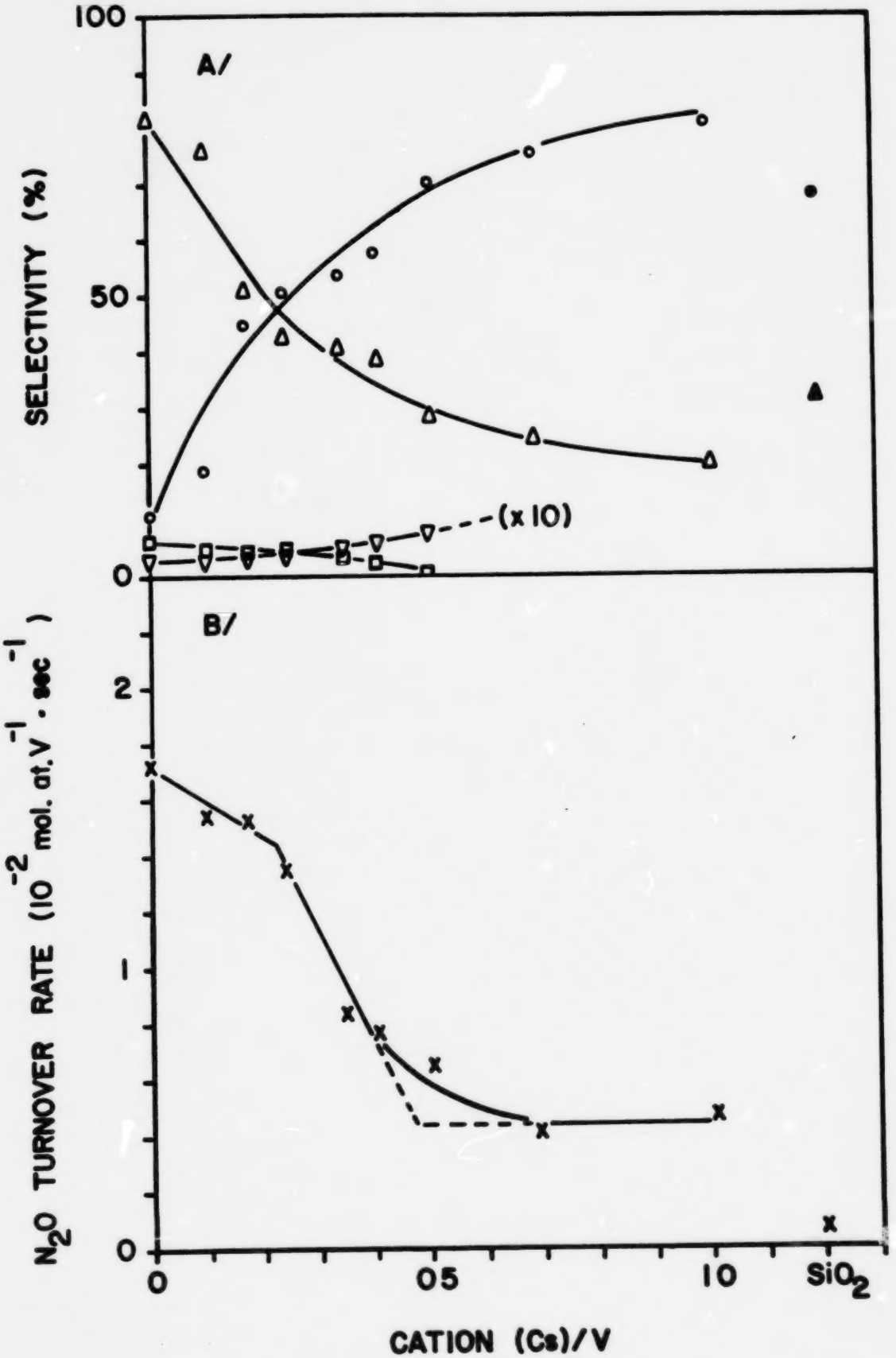
Figure 6: Turnover rate and selectivity of CH_4 oxidation by N_2O versus the amount of cesium on the 1.82 wt% Fe/SiO_2 catalyst. Same reaction conditions and symbols as figure 4.


A/
B/
100
50
0
4
3
2
1
0
(x2)
0
2
4
6
8
SiO_2
CATION (Cs)/KU (MPMo)

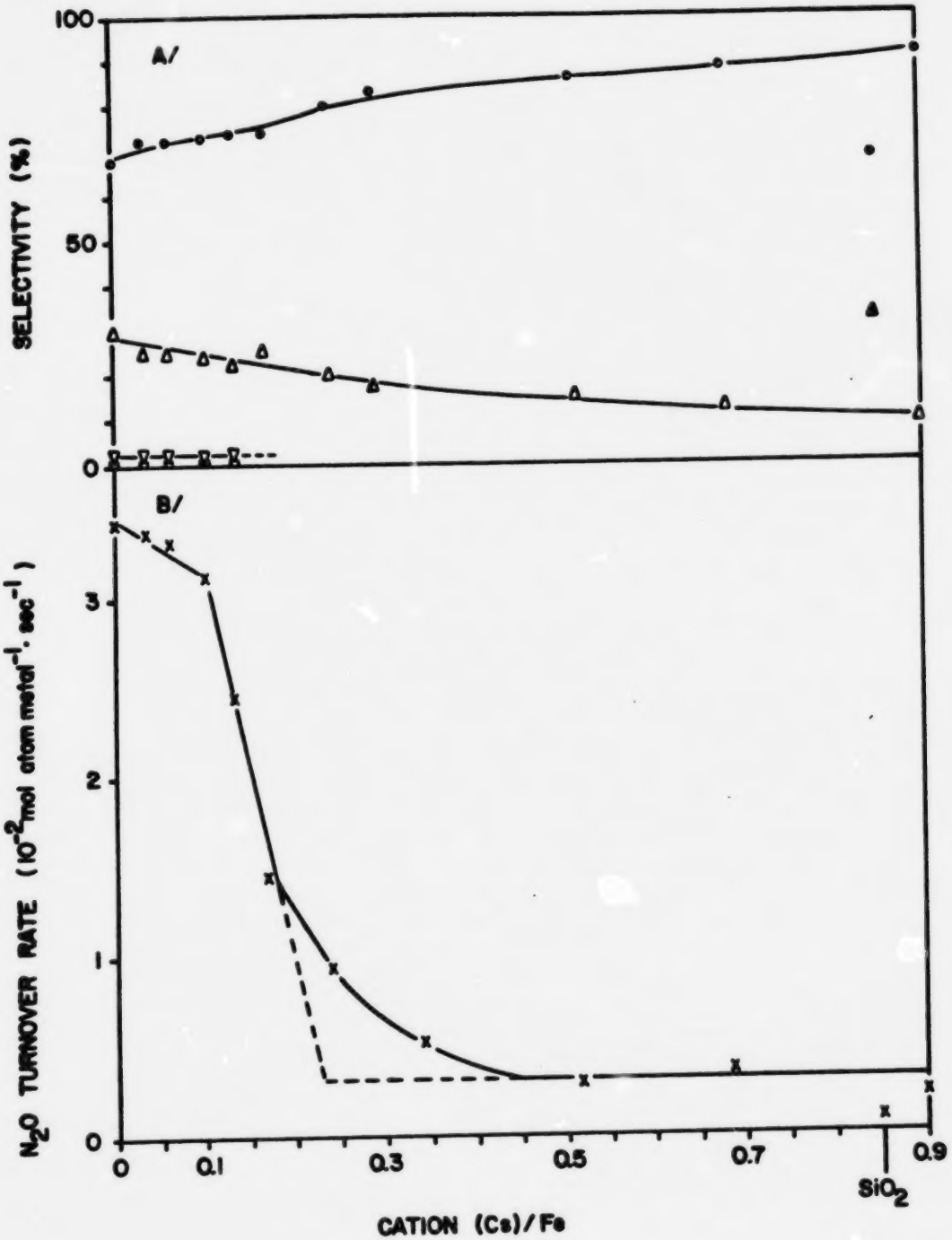

N_2O TURNOVER RATE (10^{-2}mol · KV^{-1} · sec^{-1})
SELECTIVITY (%)
HPV_2Mo_{10}
HSiMo
HPW
SiO_2
SiO_2
CATION (Cs)/ KV


A/
B/
40
30
20
10
0
20
10
0
0
2
4
6
8
SiO2
CATION (Cs) / KU (HPMo)


100
50
0
A/
SELECTIVITY (%)
B/
1.0
0.5
0
0
0.5
1.0
1.5
SiO2
CATION (Cs) / Mo



5


100
50
0
A/
SELECTIVITY (%)
B/
N_2O TURNOVER RATE (10^{-2} mol atom metal^{-1} · sec^{-1})
3
2
1
0
0
0.1
0.3
0.5
0.7
0.9
SiO_2
CATION (Cs)/Fe

THE OXIDATION OF METHANE ON HETEROPOLYOXOMETALATES

IV: PROPERTIES OF THE SILICA SUPPORTED SALTS OF 12-MOLYBDOPHOSPHORIC ACID

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ABSTRACT

Salts of 12-molybdophosphoric acid supported on silica were prepared by exchange of the supported parent acid with cesium, lithium, barium, magnesium, bismuth, aluminum, iron, silver, cobalt, chromium, copper, cadmium, mercury, nickel, lead, or vanadyl cations. The resulting solids were compared with supported 12-molybdophosphoric acid as catalysts in the oxidation of methane. Three effects due to the cations have been discerned, one attributable to the removal of protons, a second which appears to have an electronic basis, and the third related to the intrinsic activity of the cations themselves.

INTRODUCTION

Heteropoly oxometalates are ionic solids with high molecular weight cagelike anions. Although various structures are possible for the anions, those of interest here are referred to as Keggin Units. The protons of the acidic forms of these heteropoly oxometalates, such as 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) hereafter abbreviated to HPMO, can be easily, at least partly, exchanged by a large variety of inorganic or organic cations (1-4). This property allows the preparation of salts of the HPMo containing different amounts of cations and the study of the effect of these additives on the catalytic properties of these compounds. Such comparative studies on acid catalysed oxidation reactions have been reported for example by Misono et al (5) and Ai et al (6-7).

Silica supported 12-Molybdophosphoric acid has recently been shown to be an active catalyst for the partial oxidation of methane by N_2O (8). It was therefore of interest to use the exchange properties of this heteropoly oxometalate in order to investigate the properties of various supported salts of the HPMo in the partial oxidation of methane. Although the intent of this study was centered on the improvement of both the activity and selectivity of these catalysts, the possibility of fine tuning of the HPMo catalyst by doping techniques added an additional incentive for the investigation of the role of such additives.

Indeed, a preliminary study of the effect of cesium on the HPMo catalyst produced interesting structural and catalytic information (8). In particular, it has been found that cesium has two effects. First it poisoned the oxidation reaction completely for loadings higher than 3.5 Cs

per Keggin Unit (KU) apparently as a result of the substitution of the protons. This poisoning was suggested to be due to a blocking of the dehydration reaction which generates vacancies suitable for the adsorption of N_2O. Secondly, a strong electronic effect has been demonstrated to exist on partially saturated Keggin Units. Such an effect resulted in a net increase of the turnover number of the non blocked sites. Both phenomenon were also found on the supported Mo, V and Fe catalyst, an observation which emphasizes the similarity between these systems. Moreover, in the previous work (8), it was predicted that the nature of the cation should not influence the blocking effect but should influence the electronic effect. The results reported in this work clearly support that prediction and the previous conclusions reached for the cesium salts.

EXPERIMENTAL SECTION

The reaction system and conditions as well as the activation energy measurements have already been reported in detail (8). The set of reaction conditions used in the present work were: reaction temperature T_R = 843 K, catalyst weight W = 0.5 g, flow rate F = 30 mL min^{-1}, flow composition: CH_4 (67% mol), N_2O (33% mol), pretreatment: 1 hour in Helium at the reaction temperature.

The supported salts of 12-molybdophosphoric acid were prepared similarly to the cesium salt (8). The impregnation of either a 16 wt% HPMo or 23.9 wt% HPMo on silica catalysts employed solutions of the following salts: cesium carbonate (Alpha products), potassium carbonate (J.T. Baker Analysed), sodium carbonate (J.T. Baker Analysed), lithium carbonate (J.T. Baker Analysed) magnesium acetate (B.D.H.), calcium carbonate (B.D.H. Analar), strontium acetate (B.D.H.), barium acetate (J.T. Baker analysed), silver nitrate (Fisher certified), iron sulphate (B & A) or iron oxalate (BDH), bismuth nitrate (J.T. Baker analysed), copper sulphate (Fisher Certified), cadmium nitrate (J.T. Baker Analysed), manganese acetate (Fisher certified), cerium nitrate (Fisher certified), mercuric nitrate (Fisher certified), nickel nitrate (J.T. Baker Analysed), lead nitrate (B.D.H. assured), zinc nitrate (J.T. Baker Analysed), vanadyl sulphate (Fisher certified). These salts were chosen for their solubility. In some cases the salt solution was acidified by HNO_3 (1M) in order to keep a slightly acid medium and in some cases facilitate the solubilization of the salt. No major problems of precipitation have been encountered except with the bismuth impregnation.

The preparation of the cation supported on silica has also been carried out in a similar way. A loading of 0.27 cation per nm^2 of support surface has been systematically chosen, in order to correspond to the loading of 4 cations/KU samples.

The samples will be symbolized by x cation PMo with x the number of cations per HPMo Keggin unit. For the reaction conditions previously reported, the activity of the HPMo catalysts has been used as a reference with a turnover TNo = 0.044 molec. $sec^{-1}KU^{-1}$. All the activity results have been reported relative to that value.

RESULTS

The activity and selectivity of the HPMo catalyst containing increasing amounts of different cations in the reaction of methane with nitrous oxide are reported in figures 1-7. Various curves were obtained with very similar features except in those cases in which preparation problems are suspected. Most of these curves can be decomposed into three parts with discontinuities at 2 cations per KU and 3.5-4 cation per KU, the latter being followed by a plateau in the activity.

In figure 1 the results for the monovalent alkaline element cesium and lithium are reported. The results on cesium, reported here for comparison, have already been extensively discussed in a previous part (8). In that work it was concluded that on both supported heteropolymolybdate or supported oxides like Mo, V or Fe on SiO_2, the cesium ions were replacing the exchangeable protons, a phenomenon which resulted in a complete or partial poisoning of the supported HPMo or oxides, respectively. The experimental saturation value of 3.5-4 Cs/KU found with HPMo was somewhat larger than the $3H^+$ possessed by each KU of HPMo, presumably due to a difficulty in saturating all the protons of the KU and/or to the presence of some oxide from HPMo decomposition.

The selectivity variation clearly indicated that saturation of the KU was reached since the selectivity of the 4 CsPMo, 8 CsPMo, Cs/SiO_2 and SiO_2 catalysts were similar. This shows that Cs itself has no catalytic effect for the reaction and therefore the silica selectivity was reached as a result of complete poisoning. This later observation led us to conclude that the proton has an important role in the reaction mechanism of the

$CH_4 + N_2O$ reaction on the supported 12-molybdophosphoric acid. This role has been proposed as allowing the generation of vacancies by a dehydration reaction such as:

$$2\ KUOH \rightleftharpoons KUO + KU\square + H_2O \qquad (1)$$

It is apparent that the absence of protons prevents such a reaction from occurring and consequently reduces the activity where no alternative reaction is available.

The activity curve shown in figure 1a is, however, not a straight line from 0 to 3 Cs/KU as would be expected from a simple blocking effect. This was interpreted as resulting from the existence of an additional effect, believed to be electronic in origin and associated with the cesium, on the activity of the sites which can still be created on partially substituted Keggin Units. Since a higher activity than that obtained from a purely blocking effect (Figure 1a, dotted line) was observed, this electronic effect is apparently strongly positive, that is promoting.

With lithium, complete saturation could not be attained with either a large amount of this cation or two consecutive impregnations (Figure 1b). However, the portion of the curve between 0 and 2.5 Li/KU is approximately coincident with the line expected for poisoning due to a purely blocking effect, thus indicating that the electronic effect of lithium is much weaker than that of cesium. The results found for samples with 2Na and 2K per KU showed an effect intermediate to Cs and Li, the relative activity decreasing in the order Cs > K > Na > Li, corresponding to the increase of electronegativity.

In figure 2 the results for the alkaline earth elements barium and magnesium have been reported. Barium on silica shows no activity whereas magnesium develops a small activity confirmed by a selectivity very different from the support. The curve obtained with the Mg_xPMo/SiO_2 samples shows little or no evidence of failure to reach saturation since the activity and selectivity shift to the value of the Mg/SiO_2 sample for 3.5-4 Mg/KU. Interestingly, with magnesium the effect on the activity of an HPMo site which is attributed to an electronic factor is now negative, that is, poisoning. With barium, on the other hand, the activity and selectivity of the Ba/SiO_2 catalyst, equivalent to silica were not duplicated, apparently due to saturation difficulties. This problem may be illustrated by the comparison of samples prepared in different ways. A preparation involving two successive impregnations with barium acetate or a preparation with one impregnation of barium hydroxide produced samples apparently further from saturation (a and b on figure 2a). Even the preparation of a sample with a large excess of barium acetate (8Ba/KU) gave a less complete saturation than the 4 or 5.2 Ba/KU samples. The first portion of the curve can however provide information on the intensity of the electronic effect. Similar to the results found with the alkali metals, those found for samples containing 2 Ca and 2 Sr per KU are intermediate between those for Mg and Ba, leading to a decrease of the relative activity in the order Ba > Sr > Ca > Mg corresponding to the increase in electronegativity.

Two trivalent cations aluminium and bismuth were also studied (figure 3). Aluminum on silica has a net activity and a particular selectivity for the CH_4 oxidation by N_2O. Saturation of the Keggin unit appears to be

attained by 3.5-4 Al/KU while the selectivity attains the values expected for the Al/SiO_2 sample. Similarly to the observations for Mg/SiO_2 it is apparent that the HPMo Catalyst saturated with Al is equivalent to the Al/SiO_2 Catalyst. This suggests that for these cations (Mg and Al) the HPMo has no significant effect on their ability to catalyse the reaction whereas both cations have strong negative effects on the activity of the HPMo sites.

In the case of the bismuth salts the scatter of the data presumably results from difficulties either in exchanging of the protons and/or in the preparation of the samples. It was noted during the preparation that precipitation occurs. However a tentative curve has been drawn which shows that bismuth decreases the activity of the catalyst in the oxidation reaction while the selectivity clearly shows that some exchange has occurred.

The results of the influence of iron and silver on the activity and selectivity of the HPMo catalyst are reported in figure 4. In both cases we are dealing with a cation giving active species on silica, strongly active in the case of iron and slightly active in the case of silver. Again the same three parts of the curve can be distinguished with an illustration of a negative electronic effect (Fe) and a positive electronic effect (Ag). For this latter cation both the selectivity and activity reached at high loading is similar to that observed with the Ag/SiO_2 sample. This supports the idea that the exchange of all the H^+ by Ag^+ is readily accomplished. The case of iron is less conclusive. A plateau of the activity is reached but the selectivity of the FePMo catalyst, although

tending toward the value of the Fe/SiO_2 catalyst, remains noticeably different whereas the activity level of the plateau is considerably unlike that of the latter catalyst. It is likely that the Keggin unit is not completely saturated although it can be observed that two preparations from two different iron salts (oxalate and sulfate) gave similar results. A more precise look at figure 4a shows that at low iron loading a significant perturbation of the system occurred. Whether this is due to the degradation of the KU or a variation of dispersion leading to the formation of large aggregates remains unknown. In addition, the first break in the activity curve appears at 2.5-2.8 Fe/KU which is quite high compared to the 2-2.2 cation/KU obtained for many other cations, and silver in particular, and is likely to result from a non-stoichiometric saturation.

Although problems related to the structure of the catalyst generated in the preparation are again apparent in the case of iron salts, a negative electronic effect is quite evident and in contrast with the positive effect exhibited by silver salts. These results again illustrate the importance of the nature of the cation on that effect.

It can be seen in Figure 5 that the shape of the curve obtained for the effect of iron on the HPMo activity is not a unique one but occurs with many different cations. As for Fe, the Co, Cr and Cu cation on silica are very active catalysts for methane oxidation though producing no partial oxidation products for the experimental conditions used. The two other salts, cadmium and manganese on SiO_2 (Figure 5), are less active catalysts but these cations as with Fe show a large negative electronic effect

leading to a pronounced minimum of the relative activity at 2 cations per KU. In Figure 6, cerium, mercury, nickel, lead and zinc can also be seen to have a negative electronic effect but to a lesser extent. As the salts of these cations when saturated are only slightly or barely active the minimum of the relative activities is near the plateau reached after saturation.

The vanadyl salts of the different heteropoly oxometalates HPMo, 12-tungstophosphoric (HPW) and 12-tungstosilicic (HSiW) have been prepared from vanadyl sulphate and the activity and selectivity results have been reported in figure 7. Interestingly these results show that the VO^{++} cation can replace the H^+ cation and therefore strongly suggest the existence of vanadyl salts of the heteropoly oxometalates. Except for the HPMo catalyst, these salts are however not completely saturated as no plateau is reached. The inefficiency of the exchange particularly for cation loading higher than 3 Cs/KU is underlined by the difference between the properties from the preparation of two series of VOPW. A preparation with a longer saturation period gave more active catalyst after 3 VO/HPW but gave the same results for lower vanadyl loading. Interestingly the breaks appearing in the curves at c.a. 1.9 for HPMo and HPW and c.a. 2.7 for HSiW are consistent with the value expected i.e. $nH^+ - 1$ which give 2 and 3 for HPMo, HPW ($3H^+$) and HSiW ($4H^+$) respectively.

The selectivity in these three cases clearly differs from that of the unpromoted catalyst and of the VO/SiO_2 catalyst. This variation is particularly significant for HPW and HSiW with, in addition, the appearance of partial oxidation products, formaldehyde and methanol. Although no net

improvement of the selectivity relative to V/SiO_2 was found, a tendency to reach a maximum at low vanadyl contents (≈ 1.5 VO/KU) may be distinguished. The electronic effect of the vanadyl cation is negative on the three heteropoly oxometalates. Unfortunately the unsaturation does not allow comparison of the plateau levels which may have shown a possible effect of the elemental composition of the Keggin Unit on the activity of the vanadyl cation.

In order to compare the electronic effects exerted by the different cations on the HPMo catalyst properties the ratio of the turnover number of the HPMo site influenced by two cations, where the effect is maximum, over the turnover number of the original HPMo site has been computed as:

$$r = \frac{3A(2) - 2A(s)}{A(0)}$$

where A(0) is the activity of one Keggin unit, A(2), the activity of the Keggin unit saturated with 2 cations and A(s), the activity of the completely saturated Keggin unit. This latter value should be A(3) for 3 cations per KU but as experimentally observed the saturation frequently occured at higher loading. In the case of complete poisoning, evidently A(s) = 0.

Correlations of this ratio with various cation properties have been examined. That with the Pauling electronegativity of the cation is shown in Figure 8. The value of r decreases with electronegativity increase except for an apparently sharp peak in values of r for electronegativity values in the range of 1.8-2.2.

DISCUSSION

The results reported in this study support clearly the conclusions and hypotheses advanced in previous work on the structural and catalytic effects of the cations added to the HPMo catalyst. In all cases the presence of the cations modify both the activity and the selectivity of the HPMo species.

Changes in the activity and selectivity resulting from the substitution of the proton by ion exchange are evidenced particularly clearly for cesium and other cations with no intrinsic activity. Although the exchange is likely not complete in some cases (e.g. Li, Ba, Bi) it can be concluded that the saturation of the HPMo Keggin Unit occurs at 3 cations per KU regardless of the charge on the cation. The formulae of the partially stoichiometrically exchanged KU can be proposed as

$$H^{+}_{3-x}\, C^{n+}_{x}\, P\, Mo_{12}O_{40}\, A^{m-}_{\frac{n}{m}\,x}$$

with C^{n+} the cation of charge n+ and A an anion, OH^- for example, necessary to provide electrical neutrality. Evidently in the case of monovalent cations no compensating anions are necessary. The observation that the saturation occurs at approximately 3 cations per KU provides strong evidence for the Keggin Units as active species and also suggests that the three protons with HPMo and HPW or four protons with HSiW are not involved in the linkage to the silica surface. It appears then that other

modes of interaction between the Keggin Unit and the silica surface must exist. Since the Keggin Unit is a large negatively charged entity, an electrostatic interaction is one such possibility. Such an interaction is on one hand presumably relatively weak since the supported heteropoly oxometalate was readily stripped from the support by washing with acetonitrile (8), but on the other hand sufficiently strong to stabilize the structure of the supported material and increase its thermal resistance, as previously proposed (8).

The second effect on the activity produced by the introduction of cations is that interpreted here as an electronic factor. The results reported here suggest that this effect is strongly sensitive to the nature of the cation. The more electropositive or electron donating cations evidently induce an increase in turnover number whereas electron accepting cations produce a decrease of the activity. The unexpectedly high value for silver noted in Figure 8 may be due to the use of the electronegativities for the neutral atoms rather than that for the cations. It can be speculated that the increase of the electron density on the KU and particularly on the KU free sites induced by the electron donor elements such as Cs, K, Na and Li favours the formation of some active charged oxygen species symbolized previously as O* following the reaction

$$KU + N_2O \rightarrow KUO^* + N_2 \qquad (2)$$

where O* may be O^- or $O^=$ according to different authors. Since the activation energy of the reaction is not changed by the addition of cesium it appears that the rate but not the mechanism is altered. This

supports the contention that reaction 2 is the rate limiting step of the reaction.

In addition to the two effects of cations discussed above, a third factor may be discerned. With some of the cations an intrinsic activity is observed, apparently resulting from the generation of additional sites presumably operating through a reaction mechanism different from that proposed for the supported heteropoly oxometalates. This is suggested by the variation of the activation energies when the cation on saturated HPMo catalysts is changed (Table 1). Values of the activation energies found for the cations on HPMo/SiO_2 catalysts and the cations on SiO_2 catalysts are often different. Although such observations could be interpreted as evidence for the effect of the Keggin Unit on the catalytic properties of the cation it appears more probable that the structural differences between these two types of catalysts lead to different mechanisms. With the HPMo/SiO_2 catalyst the cation is presumably relatively more isolated that in the cation/SiO_2 catalysts where particles of oxides may form and lead to different catalytic behaviour.

Variation of the selectivity with cation loading generally displays three segments similar to those observed with the activity. At low loading (cation/KU$<$ 2) the selectivity changes relatively little, while at higher loading the variations are much more substantial until a stabilization is reached after the saturation of the Keggin Unit. It is of interest to note that the cations tend to increase the production of carbon dioxide at the expense of carbon monoxide except in the cases of aluminum and vanadyl cations.

In general the introduction of cations does not increase the quantities of partial oxidation products. However small amounts of bismuth, aluminum and possibly mercury and zinc cations are mildly selective for such purposes. Many other cations e.g. Cs, Li, Ba, Mg, Ag, Mn, VO, led to the generation of constant product compositions at low cation loading. However further work is required to investigate the enhancement of partial oxidation products with the HPMo catalyst and the addition of cations.

ACKNOWLEDGEMENTS

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TABLE 1

Activation Energies for Cation-Exchanged

$HPMo/SiO_2$ and $Cation/SiO_2$ Catalysts

Sample	Ea (±2 Kcal mol^{-1})	Sample	Ea (±2 Kcal mol^{-1})
HPMo	32	Mo/SiO_2	41
3CuPMo	18	Cu/SiO_2	24
3ZnPMo	40	Zn/SiO_2	28
3CrPMo	25	Cr/SiO_2	25
3CoPMo	25	---	
3NiPMo	25	---	
3FePMo	25	Fe/SiO_2	21
3VOPMo	27	V/SiO_2	34

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FIGURE CAPTIONS

Figure 1: Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of cesium carbonate (left) or lithium carbonate (right) added or the HPMo catalyst.
Open symbol and x on 16 wt% HPMo.
Black symbol and + on 23.9 wt% HPMo.
TN_0 = 0.044 molec. $sec.^{-1}$ KU^{-1}
reaction conditions T_R = 843 K, W = 0.5 g, F = 30 ml min^{-1}
CH_4 (67%) N_2O (33%)
Symbols: (Δ) CO, (0) CO_2, (□) CH_2O, (▽) CH_3OH

Figure 2: Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of Barium acetate (left) or magnesium acetate (right) on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as figure 1.
a: sample obtained by two successive impregnation of 1.5 Ba/KU
b: sample obtained by impregnation of $Ba(OH)_2$.

Figure 3: Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of Bismuth nitrate (left) or aluminum nitrate (right) on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as figure 1.
b: two successive impregnation of 1.5 Al/KU
a: preparation with aluminum isopropoxide

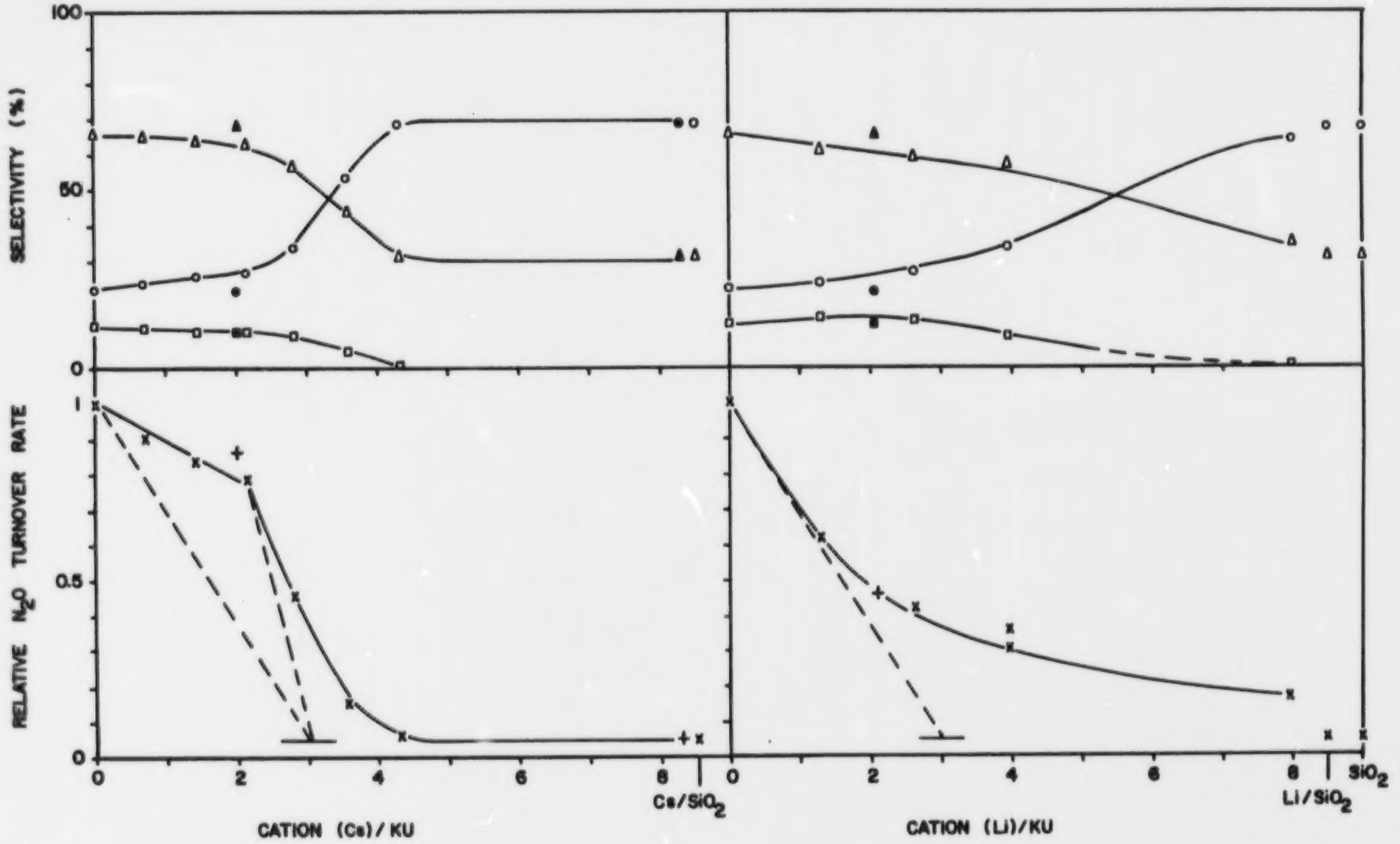
Figure 4: Relative N_2O turnover rate and selectivity of the $CH_2 + N_2O$ reaction versus the amount of iron oxalate (o) or sulphate (x) left or silver nitrate (right) on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as figure 1.

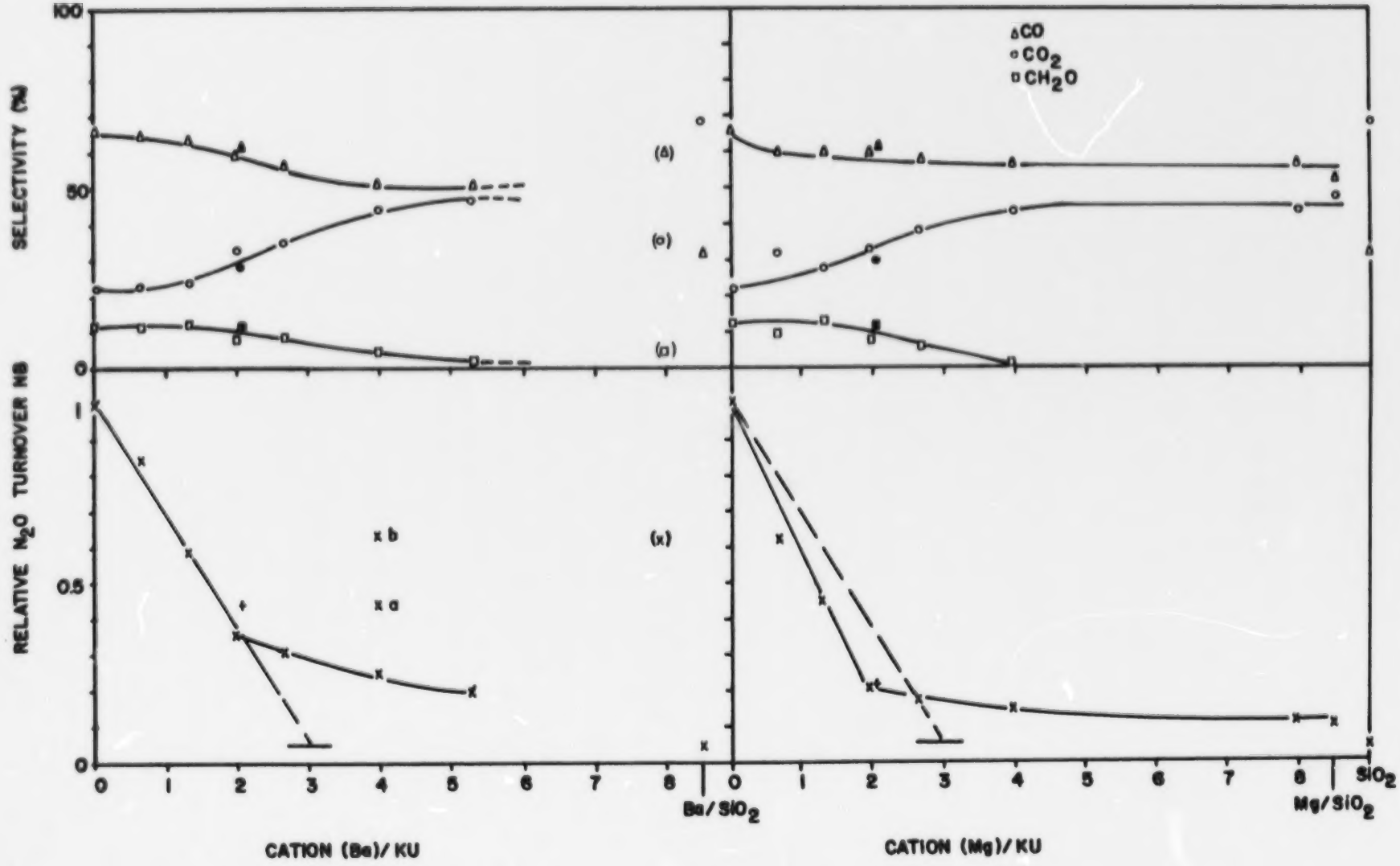
Figure 5: Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of cobalt, chromium, copper, cadmium and manganese on the 16 wt% HPMo catalyst.
Same reaction conditions and symbols as figure 1.

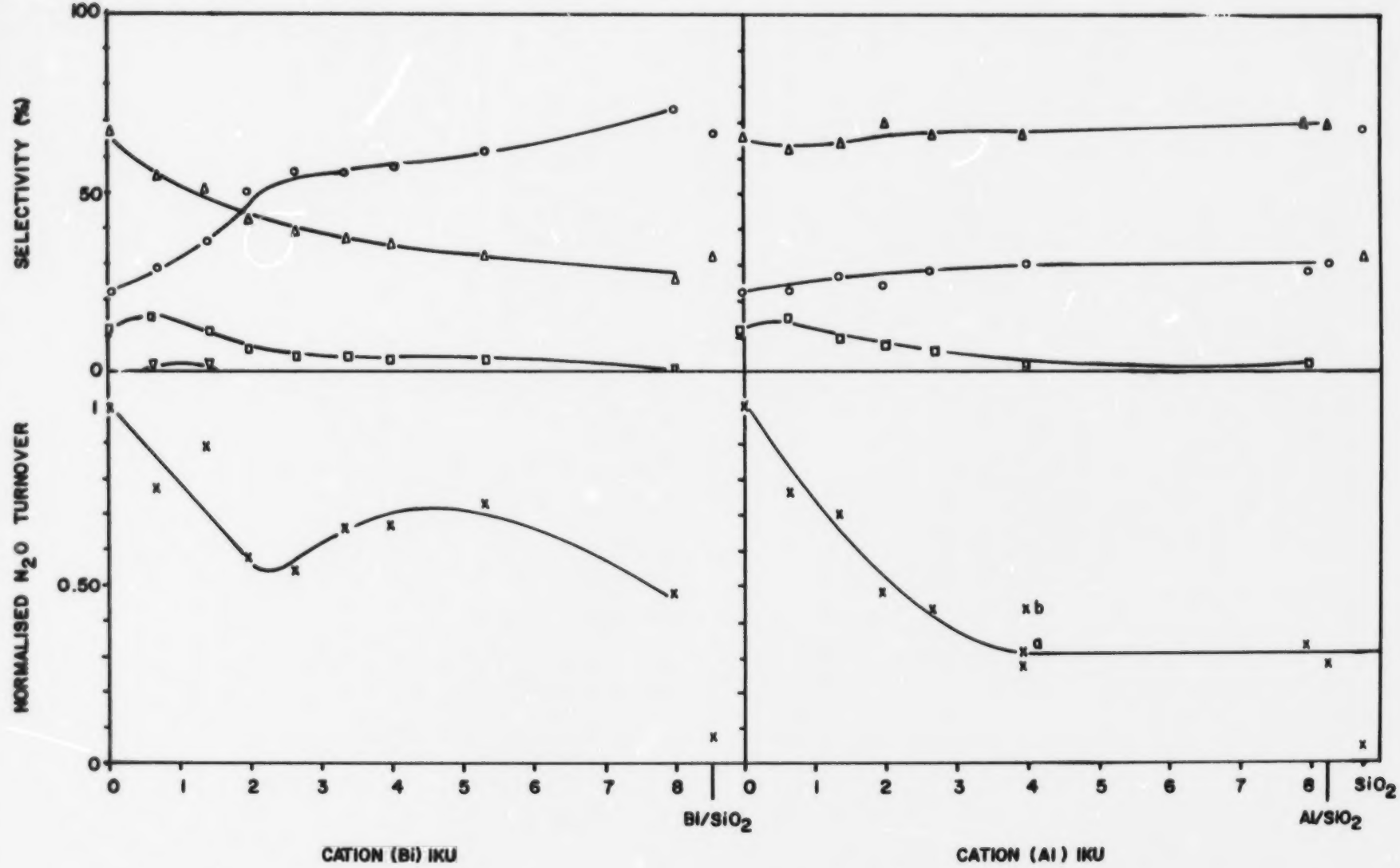
Figure 6: Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of cesium, mercury, nickel, lead, zinc on the 16 wt% HPMo catalyst.
Same reaction conditions and symbols as figure 1.

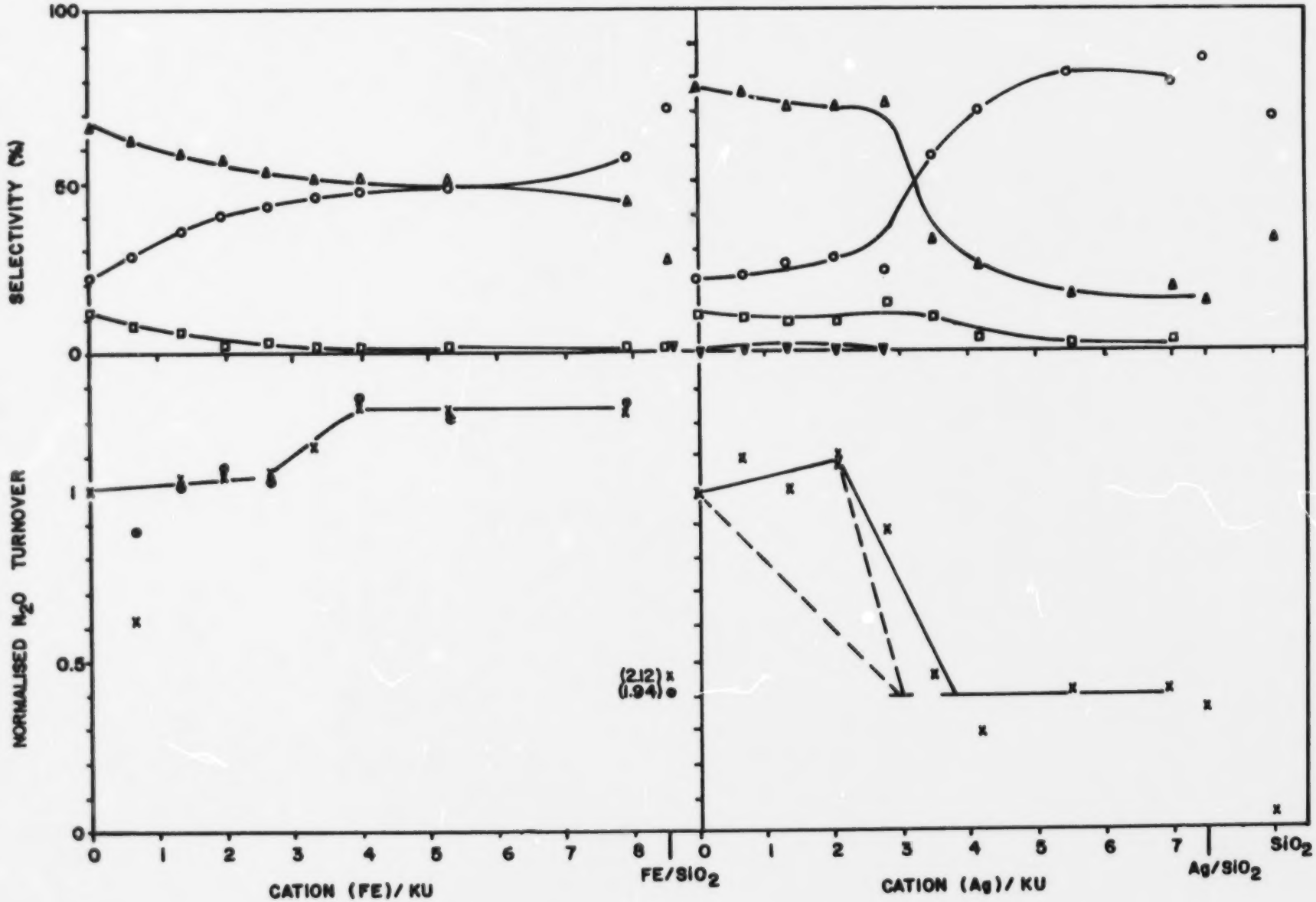
Figure 7: Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of vanadyl sulphate on the 16 wt% HPMo, 23.4 wt% HPW, 23.4 wt% HSiW catalyst. For HPW (x) first and (o) second preparation.
Same reaction conditions and symbols as figure 1.

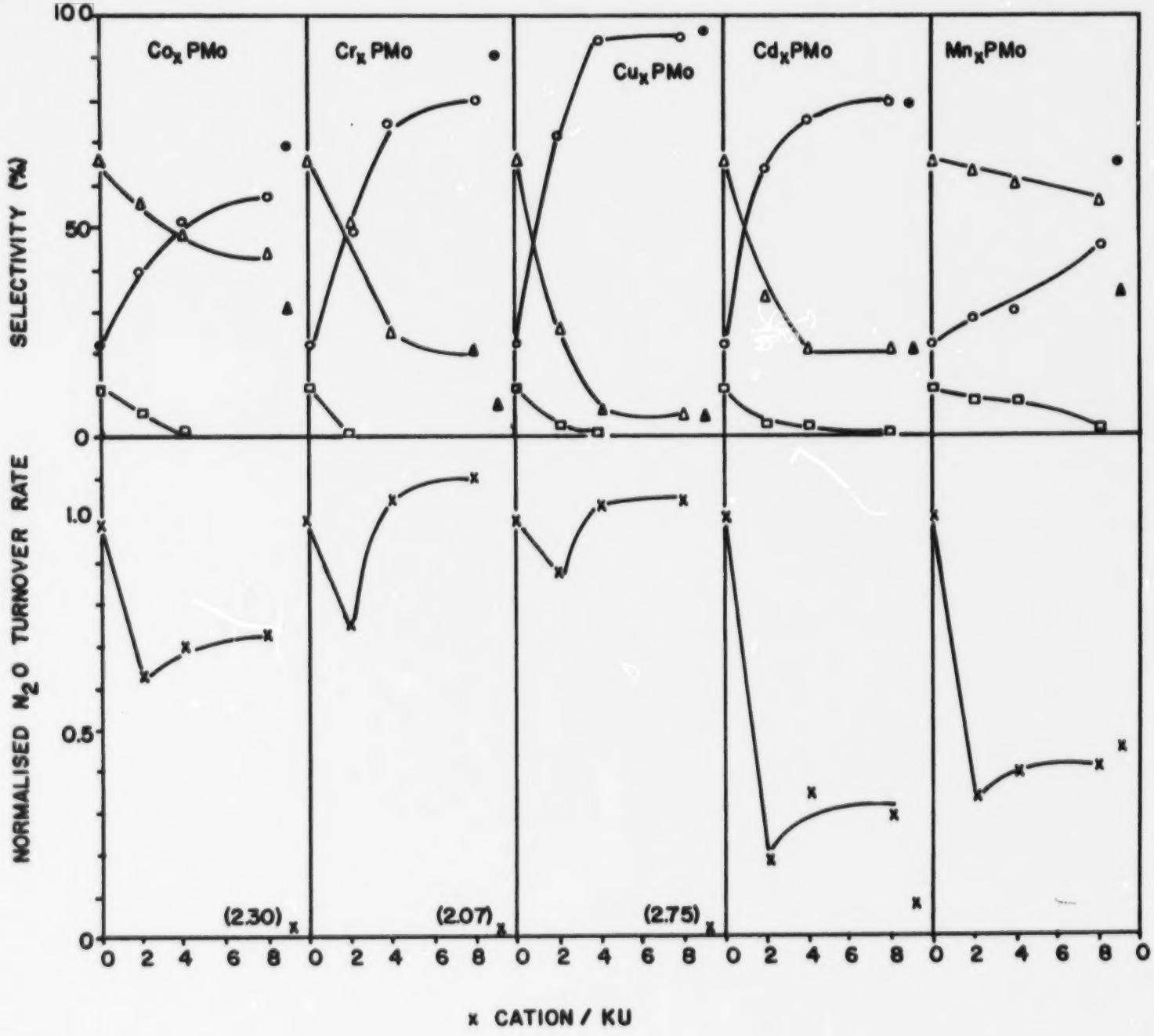
Figure 8: Relative N_2O turnover rate of the promoted site at a loading of 2 cation per KU versus the electronegativity (Pauling's scale).
( ) samples likely to be not correctly exchanged.

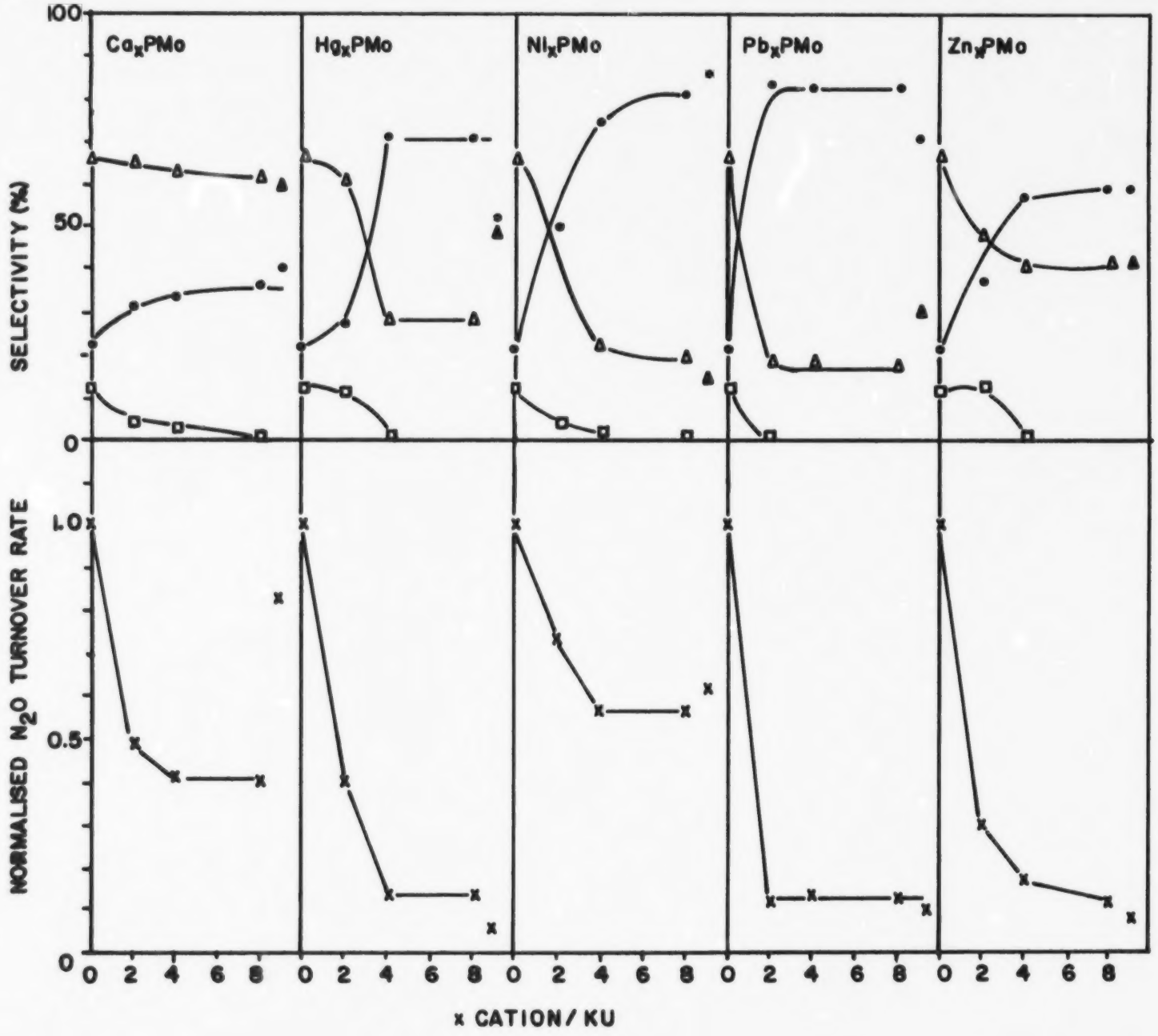

SELECTIVITY (%)
100
50
0
RELATIVE N_2O TURNOVER RATE
1
0.5
0
0
2
4
6
8
Cs/SiO_2
CATION (Cs)/KU
0
2
4
6
8
SiO_2
Li/SiO_2
CATION (Li)/KU

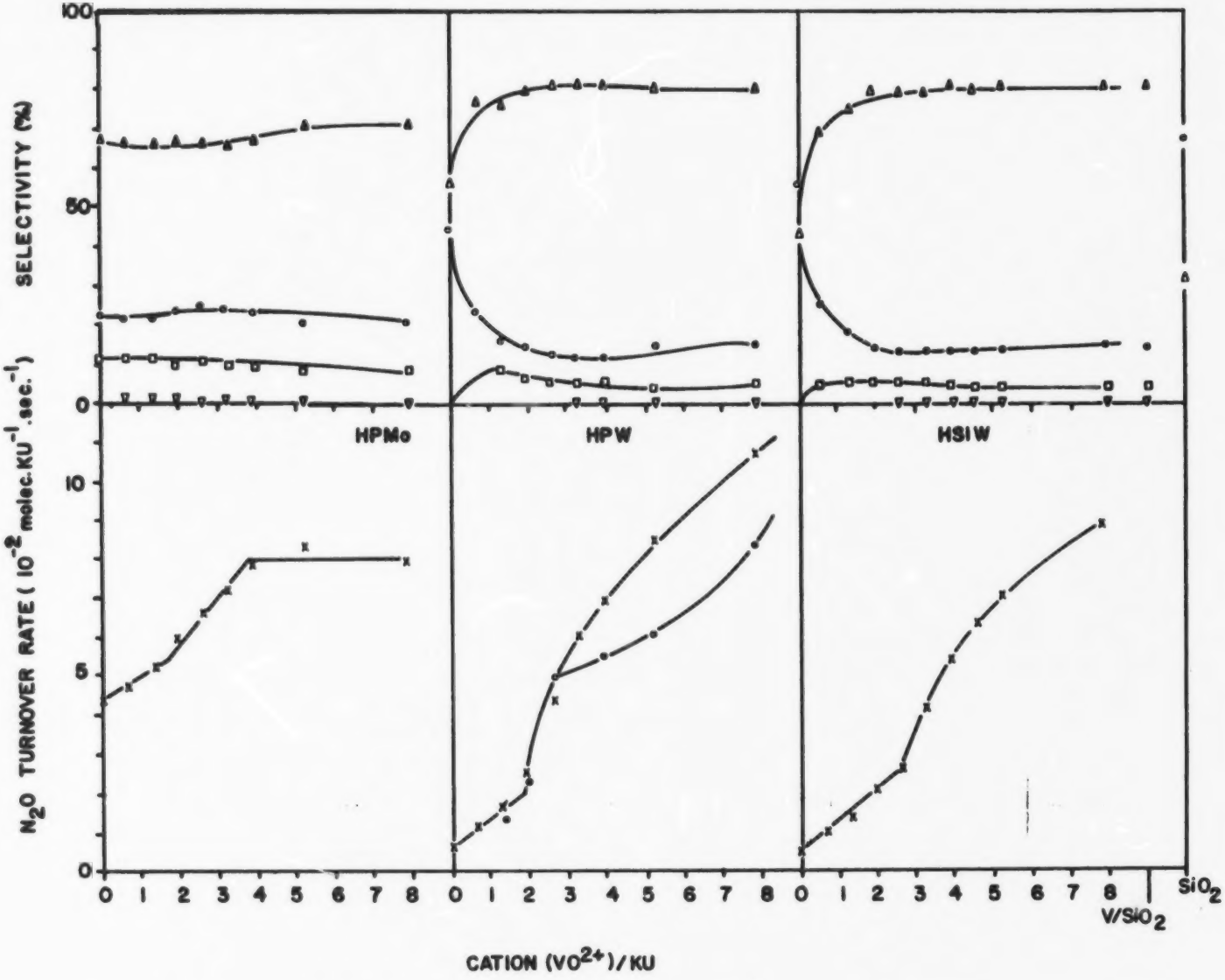

100
50
0
SELECTIVITY (%)
ΔCO
○ CO_2
□ CH_2O
(Δ)
(○)
(□)
1
0.5
0
RELATIVE N_2O TURNOVER NB
x b
x a
(x)
0 1 2 3 4 5 6 7 8
Ba/SiO_2
0 1 2 3 4 5 6 7 8
SiO_2
Mg/SiO_2
CATION (Ba)/ KU
CATION (Mg)/ KU

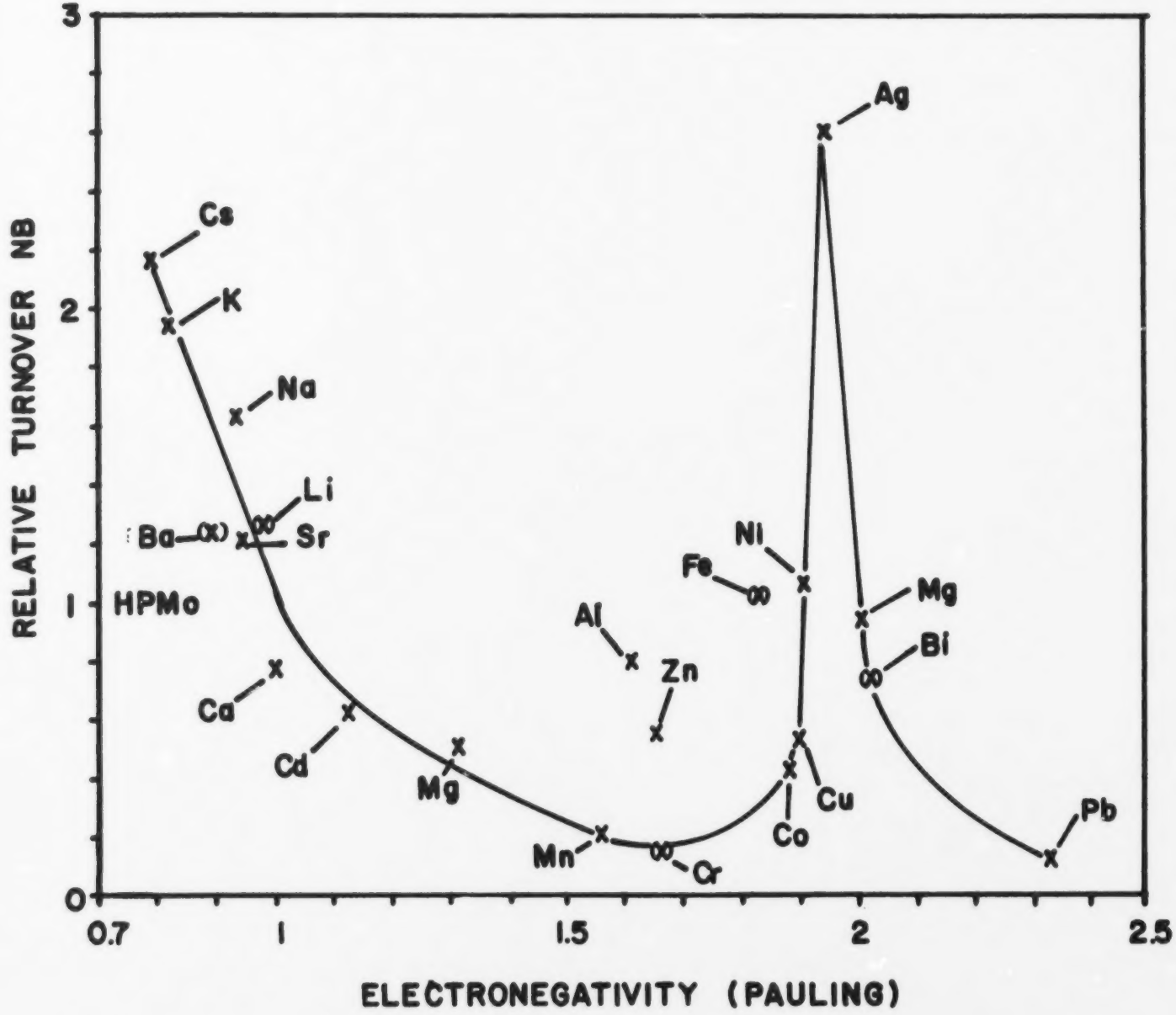

SELECTIVITY (%)
100
50
0
NORMALISED N_2O TURNOVER
1
0.50
0
0 1 2 3 4 5 6 7 8
Bi/SiO_2
CATION (Bi) IKU
0 1 2 3 4 5 6 7 8
Al/SiO_2
SiO_2
CATION (Al) IKU
b
a


100
50
0
SELECTIVITY (%)
1
0.5
0
NORMALISED N_2O TURNOVER
(2.12)
(1.94)
0 1 2 3 4 5 6 7 8
CATION (FE)/ KU
FE/SiO_2
0 1 2 3 4 5 6 7
CATION (Ag)/ KU
Ag/SiO_2
SiO_2


Co$_x$PMo
Cr$_x$PMo
Cu$_x$PMo
Cd$_x$PMo
Mn$_x$PMo
SELECTIVITY (%)
NORMALISED N_2O TURNOVER RATE
(2.30)
(2.07)
(2.75)
x CATION / KU


Ca$_x$PMo
Hg$_x$PMo
Ni$_x$PMo
Pb$_x$PMo
Zn$_x$PMo
SELECTIVITY (%)
100
50
0
NORMALISED N_2O TURNOVER RATE
1.0
0.5
0
0 2 4 6 8
x CATION / KU


100
50
0
SELECTIVITY (%)
HPMo
HPW
HSiW
10
5
0
N_2O TURNOVER RATE (10^{-2} molec.KU^{-1}.sec.$^{-1}$)
0 1 2 3 4 5 6 7 8
SiO_2
V/SiO_2
CATION (VO^{2+})/KU


RELATIVE TURNOVER NB
ELECTRONEGATIVITY (PAULING)
0
1
2
3
0.7
1
1.5
2
2.5
Ag
Cs
K
Na
Li
Ba
Sr
HPMo
Ca
Cd
Mg
Mn
Cr
Co
Cu
Ni
Fe
Al
Zn
Mg
Bi
Pb